ELECTRONICALLY FILED

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Non-Provisional Patent Application of: Inolex Investment Corporation			
Conf. No.:	Not Yet Assigned	Group Art Unit:	Not Yet Assigned
Appln. No.:	Not Yet Assigned	Examiner:	
Filing Date:	Herewith	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making The Same.		

PRELIMINARY AMENDMENT IN NEW NON-PROVISIONAL APPLICATION UNDER 37 C.F.R. 1.53(b)

Preliminary to the calculation of fees and examination of the above application being transmitted herewith, please amend the above-identified application, without prejudice, as follows:

Symrise AG, EX1004
Symrise AG v. Inolex Inc.
IPR2023-01035

Amendments to and Listing of the Claims:

Please cancel claims 42-87 without prejudice to the filing of one or more continuation or divisional applications so that the claims read as follows, with the changes as shown:

1. (original) A process for the synthesis of bio-1,2-alkanediols, comprising:

providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and

converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

2. (original) The process of claim 1, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain of about 6 to about 14 carbon atoms.

3. (original) The process according to claim 2, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain length of about 6 to about 10 carbon atoms.

4. (original) The process according to claim 3, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain length of about 6 to about 8 carbon atoms.

5. (original) The process according to claim 1, wherein the bio-alkene is bio-octene and the bio-1,2-alkane diol is bio-1,2-octanediol.

6. (original) The process according to claim 1, wherein the bio-alkene results from a process wherein a bio-1-alcohol is dehydrated by heating the bio-1-alcohol in a reactor with a catalyst.

7. (original) The process according to claim 6, wherein the reactor is a fixed bed reactor.

8. (original) The process according to claim 7, wherein the fixed bed reactor is a fluidized fixed bed reactor.

9. (original) The process according to claim 6, wherein the catalyst is selected from $ZnAl_2O_4$ and a γ-alumina catalyst.

10. (original) The process according to claim 9, wherein the bio-alkene has a bio-1-alkene regioselectivity of about 92% to about 99%.

11. (original) The process according to claim 10, wherein the bio-alkene have a bio-1-alkene regioselectivity of about 95% to about 99%.

12. (original) The process according to claim 1, wherein the process yields at least about 92% to about 99% of the bio-1,2-alkanediol.

13. (original) The process according to claim 9, wherein the catalyst is a γ-alumina catalyst is treated with a base to form a modified γ-alumina catalyst.

14. (original) The process according to claim 13, wherein the base comprises a Group I or a Group II metal.

15. (original) The process according to claim 9, wherein the γ-alumina catalyst is treated with a calcium promoter to provide a modified γ-alumina catalyst.

16. (original) The process according to claim 15, wherein the modified γ-alumina catalyst is calcined to provide a calcined γ-alumina catalyst.

17. (original) The process according to claim 16, wherein the calcium promoter is used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination.

18. (original) The process according to claim 17, wherein the calcium promoter is used in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination.

19. (original) The process according to claim 15 wherein a temperature during calcination is about 400°C to about 500°C.

20. (original) The process according to claim 19, wherein the temperature during calcination is about 420°C to about 480°C.

21. (original) The process according to claim 20, wherein the temperature during calcination is about 440°C to about 460°C.

22. (original) The process according to claim 15, wherein calcination is carried out in an oven.

23. (original) The process according to claim 15, wherein the calcination is carried out in an atmosphere of air or inert gas.

24. (original) The process according to claim 6, wherein the bio-alkene undergoes a distillation step to refine the bio-alkene prior to converting the bio-alkene to the bio-1,2-alkanediol.

25. (original) The process according to claim 6, wherein the bio-1,2-alkanediol formed from the bio-alkene undergoes a final distillation step to refine the bio-1,2-alkanediol.

26. (original) The process according to claim 1, wherein the bio-alkene results from a process wherein the bio-1-alcohol in water is dehydrated by heating the bio-1-alcohol with a catalyst under a purge gas.

27. (original) The process according to claim 1, wherein the bio-alkene is converted to the bio-1,2-alkanediol by reacting the bio-alkene in the presence of at least one of formic acid or acetic acid and a peroxide to form a bio-1,2-epoxyalkane having an epoxy ring, and contacting the 1,2-epoxyalkane with water and sodium hydroxide to form the bio-1,2-alkanediol.

28. (original) The process according to claim 1, wherein the process yields at least about 60% to about 99% of the bio-1,2-alkanediol.

29. (original) The process according to claim 28, wherein the process yields at least about 72% to about 99% of the bio-1,2-alkanediol.

30. (original) A process for making bio-1,2-alkanediols, comprising:

providing a bio-1-alcohol and a catalyst treated with a base;

dehydrating the bio-1-alcohol in the presence of the catalyst to form a bioalkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and

converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

31. (original) The process according to claim 30, wherein the catalyst is a γ-alumina catalyst and the base comprises calcium.

32. (original) The process according to claim 31, wherein the γ-alumina catalyst is treated with a calcium promotor and after treatment is calcined at a temperature of about 400°C to about 500°C.

33. (original) The process according to claim 30, wherein the process yields about 72% to about 99% of the bio-1,2-alkanediol.

34. (original) The process according to claim 30, wherein the bio-1-alkene regioselectivity is about 95% to about 99%.

35. (original) A method for treating a catalyst for use in dehydration of alcohols, comprising

providing a γ-alumina catalyst;

treating the γ-alumina catalyst with a base comprising a Group I or a Group II metal; and

heating the γ-alumina catalyst to a temperature of about 400°C to about 500°C.

36. (original) The method according to claim 35, wherein the base comprises calcium.

37. (original) The method according to claim 36, wherein the base is a calcium promoter and the heating occurs during calcination.

38. (original) The method according to claim 37, wherein the calcium promoter includes is used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination.

39. (original) The process according to claim 38, wherein the calcium promoter is used in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination.

40. (original) The process according to claim 35, temperature during calcination is about 420°C to about 480°C.

41. (original) The process according to claim 40, wherein the temperature during calcination is about 440°C to about 460°C.

42. - 87. (canceled)

REMARKS

Claims 1-41 are presently pending in this application.

Claims 42-87 have been canceled without prejudice to the filing of one or more divisional or continuation applications.

No new matter has been added by these amendments, and entry thereof and an early notice of allowance are respectfully requested.

Respectfully submitted,

INOLEX INVESTMENT CORPORATION

1/30/19 By: _____

(Date)

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LLC:llc

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	lynda Leigh Calderone
Attorney Docket Number:	I0113-198U1

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	300	300
UTILITY SEARCH FEE	1111	1	660	660
UTILITY EXAMINATION FEE	1311	1	760	760
Pages:				
Claims:				
CLAIMS IN EXCESS OF 20	1202	21	100	2100
Miscellaneous-Filing:				
LATE FILING FEE FOR OATH OR DECLARATION	1051	1	160	160

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**3980**

Electronic Acknowledgement Receipt

EFS ID:	35013735
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	159443
Filer:	lynda Leigh Calderone
Filer Authorized By:	
Attorney Docket Number:	I0113-198U1
Receipt Date:	30-JAN-2019
Filing Date:	
Time Stamp:	23:33:15
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$3980
RAM confirmation Number	013119INTEFSW23345500
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	transmittal.pdf	145664 3cdf0bed20be3072de6b27d46a7e40918a62a619	no	3
Warnings:					
Information:					
2	Application Data Sheet	ADS198U1.PDF	1304793 e24332d93ae99f05c25cd5f968c29f2799a45d05	no	9
Warnings:					
Information:					
3		nonprovisional.pdf	409355 44a4f47a57522d504a9892c144958f5cc304c013	yes	50

Multipart Description/PDF files in .zip description

Document Description	Start	End
Specification	1	41
Claims	42	49
Abstract	50	50

Warnings:					
Information:					
4	Drawings-only black and white line drawings	drawings.pdf	95739 172034af12ce29fdd7c44114bb3a2e887a562bac	no	7
Warnings:					
Information:					
5	Oath or Declaration filed	Declaration198U1.pdf	101722 ffdaaa446c28643e9ff8a1e9e4d7e09a379e0481	no	3

Warnings:					
Information:					
6		prelamend.pdf	232643 1105667f4df7d7a06e6cac964ab639cbd68ea144	yes	6
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Preliminary Amendment		1	1	
	Claims		2	5	
	Applicant Arguments/Remarks Made in an Amendment		6	6	
Warnings:					
Information:					
7	Fee Worksheet (SB06)	fee-info.pdf	38677 311c5765ed11b9cae309b2e2eee21477bbbdf742	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	2328593		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

NON-PROVISIONAL
UTILITY PATENT APPLICATION
TRANSMITTAL - 37 CFR 1.53(b)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Attorney Docket No.: I0113-198U1
First Named Inventor: Rocco Burgo
ELECTRONICALLY FILED
Applicant Name: Inolex Investment Corporation
Total Pages of Transmittal Form: 3

Transmitted herewith for filing is the non-provisional utility patent application entitled:

NATURAL 1,2-ALKANEDIOLS, COMPOSITIONS HAVING NATURAL 1,2-ALKANEDIOLS AND PROCESSES FOR MAKING THE SAME

which is:

an **[X]** Original; or

a [ ] Continuation, [ ] Divisional, or [ ] Continuation-in-part (CIP) of prior U.S. Non-Provisional Patent Application No. _____, filed ____.
Anticipated Group/Art Unit: ___ or Class _____, Subclass ____.

[ ] This non-provisional patent application is based on Provisional Patent Application No. 62/623,985, filed January 30, 2018.

Enclosed are:

[X] Specification (including Abstract) and claims: 50 pages.

[X] 7 sheets of drawings (formal).

[X] Application Data Sheet Under 37 C.F.R. 1.76.

[X] Unexecuted: [ ] Inventor Declaration; [ ] Inventor Declaration and Power of Attorney; [ ] Inventor Oath; [ ] Substitute Statement.

[ ] Copy of [ ] Declaration; [ ] Declaration and Power of Attorney from prior application.

[ ] Copy of separate Power of Attorney (including 37 CFR 3.73(b) statement, if applicable).

[ ] Microfiche computer program (Appendix).

[ ] Nucleotide and/or Amino Acid Sequence Submission, including:

[ ] Computer readable copy [ ]Paper Copy [ ] Verified Statement.

[X] Name of Assignee: Inolex Investment Corporation

[ ] Certified copy(ies) of ____ Application No(s). _____ filed ____ is/are filed:

[ ] herewith or [ ] in prior application _____.

[ ] Applicant(s), by its/their undersigned attorney, claim(s) Small Entity Status under 37 C.F.R. §1.27 as [ ] an Independent Inventor, or [ ] a Small Business Concern, or [ ] a Non-Profit Organization.

[X] **Preliminary Amendment.**

[ ] Information Disclosure Statement, PTO/SB/08A or B, and cited references.

[ ] Request for Nonpublication of Application Under 35 U.S.C. §122(b)

[ ] Other:

The filing fee is calculated as follows:

			MICRO ENTITY			SMALL ENTITY			LARGE ENTITY	
CLAIMS	NO. FILED	NO. EXTRA	BASIC FILING, SEARCH, AND EXAMINATION FEES:	$430		BASIC FILING, SEARCH, AND EXAMINATION FEES:	$ 785		BASIC FILING, SEARCH, AND EXAMINATION FEES:	$1,720
Total	41-20 =	21	X $ 25	$	OR	X $ 50	$	OR	X $100	$2,100
Independent	3 - 3=	0	X $115	$	OR	X $230	$	OR	X $460	$0
[0] Multiple Dependent Claims			X $205	$	OR	X $410	$	OR	X $820	$0
[ ] Application Size Fee (if specification and drawings exceed 100 sheets)										
Total sheets	-100	Add'l sheets =	# of sets of 50 (round up to whole number) /50 =	X $100 =	$	OR	X $200 =	$	OR	X $400	$0
Late Fee For Filing Fees, Inventor Oath or Declaration			$ 40	$	OR	$ 80	$	OR	$160	$160
Late Fee For Non-English Specification			$ 35	$	OR	$ 70	$	OR	$140	$0
			TOTAL	$	OR	**TOTAL**	$	OR	**TOTAL**	$3980

[ ] **The Commissioner is not authorized to charge the filing fee at this time as we elect to defer payment of the entire filing fee until receipt of a Notice to File Missing Parts**

[X] Applicant herewith charges the above-noted filing fees in the amount of $___ as calculated above to the credit card account, Calderone Bullock American Express (Billing No. I0113.0249).

[X] The Commissioner is hereby authorized to charge and/or credit Deposit Account No. 60-2682 (Billing No. I0113.0249) as noted below.

[ ] Any overpayments or deficiencies in the above-calculated fee.

[ ] Any additional fees required under 37 C.F.R. § 1.16 and § 1.17.

[X] In the event that a Petition for Extension of Time is required during the prosecution of this application, but not submitted, please charge any extension fee under 37 C.F.R. § 1.136(a) to our Deposit Account noted above.

CORRESPONDENCE ADDRESS

1/30/19 By: _____

(Date)

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[X] Customer Number or Bar Code Label: **000159443**

LLC:llc
Enclosures: Preliminary Amendment

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
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Residence Information (Select One) ● US Residency Non US Residency Active US Military Service

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Address 2	

City	State/Province	Postal Code	Country
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Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
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Residence Information (Select One) ◉ US Residency Non US Residency Active US Military Service

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Mailing Address of Inventor:

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Address 2	

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Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Gary	B.	Mosser	

Residence Information (Select One) ◉ US Residency Non US Residency Active US Military Service

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

City	Tabernacle	State/Province	NJ	Country of Residence	US

Mailing Address of Inventor:

Address 1	5 Colonial Court		
Address 2			
City	Tabernacle	State/Province	NJ
Postal Code	08088	Country	US

Inventor 4 — Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Michael	J.	Fevola	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Belle Mead	State/Province	NJ	Country of Residence	US

Mailing Address of Inventor:

Address 1	409 Township Line Road		
Address 2			
City	Belle Mead	State/Province	NJ
Postal Code	08502	Country	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	159443		
Email Address	USP@calderonebullock.com	Add Email	Remove Email

Application Information:

Title of the Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same		
Attorney Docket Number	I0113-198U1	Small Entity Status Claimed	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	7	Suggested Figure for Publication (if any)	1

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	159443		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Claims benefit of provisional	62623985	2018-01-30

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

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B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 — Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	Inolex Investment Corporation		
Mailing Address Information For Applicant:			
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City	Wilmington	**State/Province**	DE
Country	US	Postal Code	19810
Phone Number		Fax Number	
Email Address			

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Assignee Information including Non-Applicant Assignee Information:

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Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

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Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
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Signature:

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NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

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See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Lynda L. Calderone/			Date (YYYY-MM-DD)	2018-01-30
First Name	Lynda L.	Last Name	Calderone	Registration Number	35837

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	I0113-198U1
	Application Number	
Title of Invention	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3 A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent CooperationTreaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

TITLE OF THE INVENTION

[0001] Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making The Same.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] This U.S. Non-Provisional Patent Application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Patent Application No. 62/623,985, filed January 30, 2018, entitled, "Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Methods of Making Same," the entire disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0003] The invention herein relates to the field of natural and renewable, *i.e.*, sustainable, antimicrobial components that enable alternative preservation systems for use in compositions applicable to various industries, including personal care, household and institutional or industrial cleaning products, medical or other related uses, and particularly in personal care compositions. More particularly to the preparation of natural and renewable 1,2-alkanediols, methods for making natural and renewable 1,2-alkanediols and compositions including such 1,2-alkanediols prepared from natural and renewable ("sustainable") feedstocks.

DESCRIPTION OF RELATED ART

[0004] In most countries, including the United States, cosmetic and/or personal care ("personal care products") and other consumer products are manufactured and packaged in clean, but not typically sterile conditions, and many are sold in non-sterile forms. As a result, inconsequential (and usually harmless) amounts of bacteria, mold or yeast spores (collectively, "microbes") may be caught in products. In addition, once a consumer has purchased, opened and begun using such a product, further contamination may occur. For example, in personal care products, small amounts of microbes from the air or a consumer's skin may further contaminate the product.

[0005] Over time, during transit, storage or use the initial microbe population that was negligible may increase to a level significant enough to result in discoloration or fouling of the

product, including the appearance of visible mold, which can impact the usefulness or performance of the product. In the case of personal care products or other consumer products that are applied or ingested (such as vitamins, etc.), it can have a health impact as well, and in some circumstances can lead to adverse skin reactions upon application, including infection.

[0006] To address the issue of microbial growth, manufacturers in the personal care industry and in other industries commonly add chemical preservatives, which are typically petrochemically based, to such products and compositions. However, the type and amount of preservative that can be used is subject to restrictions on several fronts: (1) legislative (in some countries, use of particular preservatives are prohibited); (2) technical (the type/amount of preservative must demonstrate its efficacy by meeting certain empirically assessed criteria ("challenge testing"); (3) consumer preference (consumers may perceive certain preservative chemicals as undesirable, such as petroleum-based or non-sustainable products, so products including them are not commercial viable); (4) logistical (*e.g.*, the selected preservative must be effective in the relevant chemical environment (where parameters such as pH, hydrophobicity/hydrophilicity, etc. may vary) and production-cost friendly); and (5) sustainability, *i.e.*, it should be prepared using sustainable processes and feedstock sourcing as described further herein.

[0007] There is also a desire to develop alternatives to traditional preservation and to find more user-friendly chemical component combinations that are derived from sustainable and renewable resources (*i.e.*, "feedstocks"). These natural and renewable antimicrobial components and alternatives to traditional preservatives ("alternative preservation"), should provide equal or better protection and performance to the consumer.

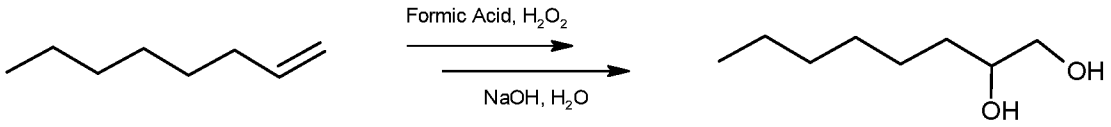
[0008] To resolve issues with traditional preservatives, the applicant herein developed a prior art preservative for personal care compositions that does not include parabens, formaldehyde donors or chlorinated compounds, that can be used in all types of personal care formulations (*e.g.*, both "leave-on" and "rinse-off" products). Such paraben-free or other non-petroleum-based alternative preservation products are attractive to consumers. The paraben-free preservative demonstrates efficacy against a broad spectrum of microorganisms at various levels of pH, especially around neutral pH levels which hare typically in or on the human body. This preservative is described in U.S. Patent Publication No. 2017/0360035 A1, in which one of the components in that preservative system is a 1,2-alkanediol.

[0009] Another attempt in the art to reduce the use of traditional preservatives is in the application of "hurdle technology." Hurdle technology is the practice of applying several types of restricting or preservative materials or processes so that microbes have a "hurdle(s)" to overcome before they can proliferate to spoilage levels (e.g., adding something to change pH to reduce proliferation and a smaller amount of preservative or other compound that together retard or create "hurdles" to microbial growth). Use of alternative preservation can be one step or "hurdle" in hurdle technology.

[0010] There is a need in the art to further develop "alternative preservation" additives. These alternative preservation systems include consumer-friendly, paraben-free materials that move away from traditional preservation or antimicrobials and towards "natural" and "sustainable" ("renewable") formulations and feedstocks, as those terms are defined hereinbelow.

[0011] One diol employed in preservation, caprylyl glycol, is believed by the applicant to be the fastest growing alternative preservation component in the world. Other 1,2-alkanediols such as 1,2-hexanediol, 1,2-decanediol, and 1,2-dodecanediol are also growing in popularity and function in alternative preservation formulations.

[0012] An example of one reaction sequence to prepare caprylyl glycol (1,2-octanediol) using an alkene as a key starting material is shown below. The starting material used is a petrochemically-derived 1-octene:



petroleum-based 1-octene

petroleum-based 1,2-octanediol

In the above reaction sequence, a petrochemically-derived 1-octene is reacted in the presence of formic acid and peroxide to form an intermediate chemical mixture which, e.g., undergoes a further ring-opening reaction in water with sodium hydroxide to complete formation of the 1,2-octanediol. This provides an excellent alternative preservation additive and is paraben-free, however, the starting material (*i.e.*, 1-octene) is derived from a fossil-based (petrochemical) resource and importantly, represents a non-renewable feedstock, *i.e.*, a non-sustainable resource.

[0013] Thus, as noted above there is a need for more consumer- and eco-friendly, alternative preservation systems (used alone or as part of hurdle technologies), including those that are paraben-free. There is further a need in the art for a material that is an alternative preservation material or that may be used in an alternative preservation system that is a 100% natural and renewable ("sustainable") feedstock to create an antimicrobial agent that can be used as or in alternative preservation systems. An example of a "natural" antimicrobial is one that is prepared from a bio-derived feedstock (*e.g.*, from current and sustainable agricultural activities, like non-GMO based-fermentation, algae-, plant- or vegetable-derived, *e.g.*, it comes from vegetable sources, or biomass, and it is not petrochemically-derived (such as being derived from sustainable tree and plant farms active in the 21st century). Such feedstocks are referred to herein as "natural" and "renewable" (*i.e.*, "sustainable") and are known as a non-petroleum-derived feedstock. Further, such materials are formed by "new" carbon and not from petroleum or other fossil fuel sources ("old" carbon). Such products are referred to herein as "natural" products and are known in the art as non-petrochemically-derived or "bio" products. By "sustainable," herein, the applicants are referring to materials that come from renewable sources, and not those that deplete a limited natural resource, such as a fossil fuel or other non-renewable resource such as petroleum. Thus a natural or bio product, which is not petrochemically derived, and/or is made from sources that are not petrochemically derived would be sustainable and renewable.

[0014] True natural products (bio-compounds) are formed using biomass (*e.g.*, material stored from carbon cycle processes in living plants and roots, etc. or released through animal respiration or through decomposition). When carbon decomposes and is broken down over millions of years under pressure, it creates fossil fuels (the source of petrochemically-derived carbon). Bio-compounds herein are intended to include materials derived from the carbon of plant sources/biomass, that exist recently and are also sustainable, and are not derived from fossil fuels.

[0015] These bio-based or "natural" feedstocks may be used in the production of alternative preservation formulations. The bio-based or "natural" products from such feedstocks may be tested to determine that they come from a true, natural and sustainable (as those terms are defined herein) feedstock source. Some products are known or advertised as being from natural sources when, in fact, they may not be prepared from truly natural and/or sustainable feedstock. A natural organic product is typically defined as a compound produced naturally by a living

organism. To distinguish a petroleum-based product from a truly natural and/or sustainable product, one must test for the authenticity using established and credible test methods. The most current method employs a detailed analysis of stable isotopes using mass spectroscopy and evaluating carbon-12/carbon-13 and/or hydrogen-1/hydrogen-2 ratios. Such testing is available through several analytical service testing organizations and is much faster, more cost effective, and yields more detailed information compared to radiocarbon testing methods.

[0016] Stable isotope analysis is based on the principle of kinetic isotope effect. The latter effect is well-known to those in the art of chemical kinetics. In the broadest terms, heavy isotopes of a particular element react slower than their lighter equivalent (*e.g.*, carbon-12 as opposed to carbon-13). So, as plants incorporate carbon dioxide into their biomass, the ratio of carbon-12 to carbon-13 will vary depending on the type of chemistry used in the plant to make biomass (*e.g.*, whether the plant undergoes a C_3 or C_4 photosynthesis pathway). This is commonly reported as the $\delta^{13}C/^{12}C$ ratio (*i.e.*, $\delta^{13}C$), and is referenced to a current carbon dioxide standard. In addition, similar isotope kinetic effects are observed when water is incorporated into new biomass, and this is measured as the $\delta^{2}H/^{1}H$ ratio (*i.e.*, $\delta^{2}H$). Using a combination of $\delta^{13}C$ and $\delta^{2}H$ ratios, one familiar with in the relevant art is able to readily distinguish and validate the nature of the feedstock that was used to prepare the product being analyzed (*i.e.*, whether it is petrochemically-derived or derived from recently living or living algae-, plant- or similar bio-sources).

[0017] In Fig. 2, it can be seen in general terms how isotope ratios can be used to determine the source of various detergents that have a strong relation to the feedstocks described herein, like 1-octanol. From the plot in Fig. 2, the $\delta^{2}H$ values have a more clearly defined difference between petroleum-based and renewable feedstocks and so in this case prove more valuable and defining than the $\delta^{13}C$ values. However, the combination using $\delta^{2}H$ and $\delta^{13}C$ values together is a preferred technique employed in the invention herein to prove a feedstock is, in fact, natural and renewable.

[0018] Radiocarbon is an unstable isotope of carbon, known as ^{14}C. ^{14}C is an unstable isotope that emits radiation energy in the form of *beta* particles at a very consistent rate and

ultimately decays to the more stable ^{14}N (*i.e.*, a half-life for radiocarbon is 5730 years). Because petroleum-based (*i.e.*, petrochemically-derived) feedstocks are derived from plants and animals buried millions of years ago, the feedstocks' radiocarbon (*i.e.*, ^{14}C) has been lost to decay. The ASTM International standards provide testing standards to determine the authenticity of a "bio-based compound" using radiocarbon, which may be found in ASTM D6866-16. This standard distinguishes newer carbon from carbon derived from fossil-fuel, or petroleum- and petrochemically-derived sources, *i.e.*, "old carbon." The amount of ^{14}C in recent or current biomass is known, so a percentage of carbon from a renewable source can be estimated from a total organic carbon analysis, which provides the data necessary to determine if a compound is truly derived from a "natural" and/or "sustainable" ("renewable") feedstock source or is derived conversely from a compound of "old" sequestration (*i.e.*, a petrochemically-derived or petroleum-based source). The use of petroleum-based or often labeled fossil-based feedstocks is generally accepted as being non-sustainable, *i.e.*, old carbon is a non-sustainable and not a renewable feedstock, and furthermore, is not considered "natural" and "sustainable" in the art. As defined herein, it would not be considered to be a "natural" product or useful in a "natural" formulation. Hence, use of such feedstocks does not represent a path forward to development of "natural" and "renewable" alternative preservatives.

[0019] Dehydration of terminal alcohols using traditional methods to form alkene starting materials chemically yields a mixture of 1- alkenes, 2- alkenes, and 3- alkenes due to rearrangements and migrations of the 1-alkene product during the dehydration process. Using such a mixture of alkenes ultimately provides a mixture of diols upon dihydroxylation, providing a low yield of the desired terminal 1,2-diol material and unwanted contaminants.

[0020] In one known path of forming caprylyl glycol (1,2-octanediol) starting with 1-octanol, made from petrochemically-derived (*i.e.*, petroleum-derived or fossil fuel-derived) feedstocks, the following reaction is known to occur:

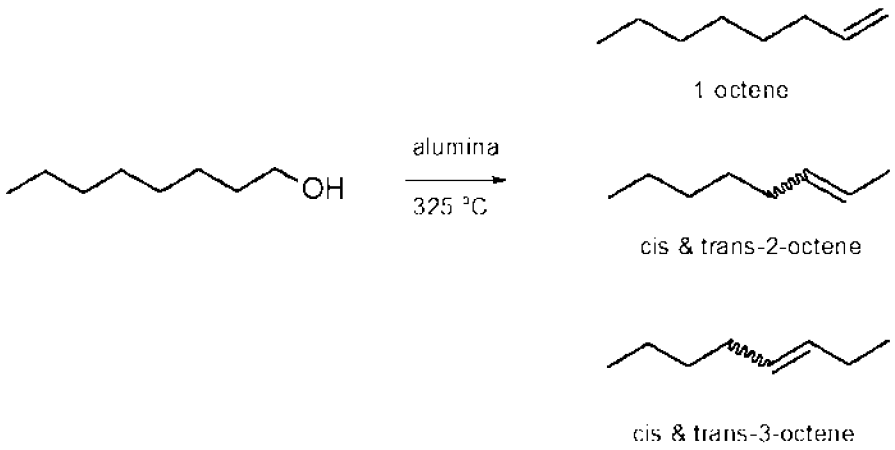
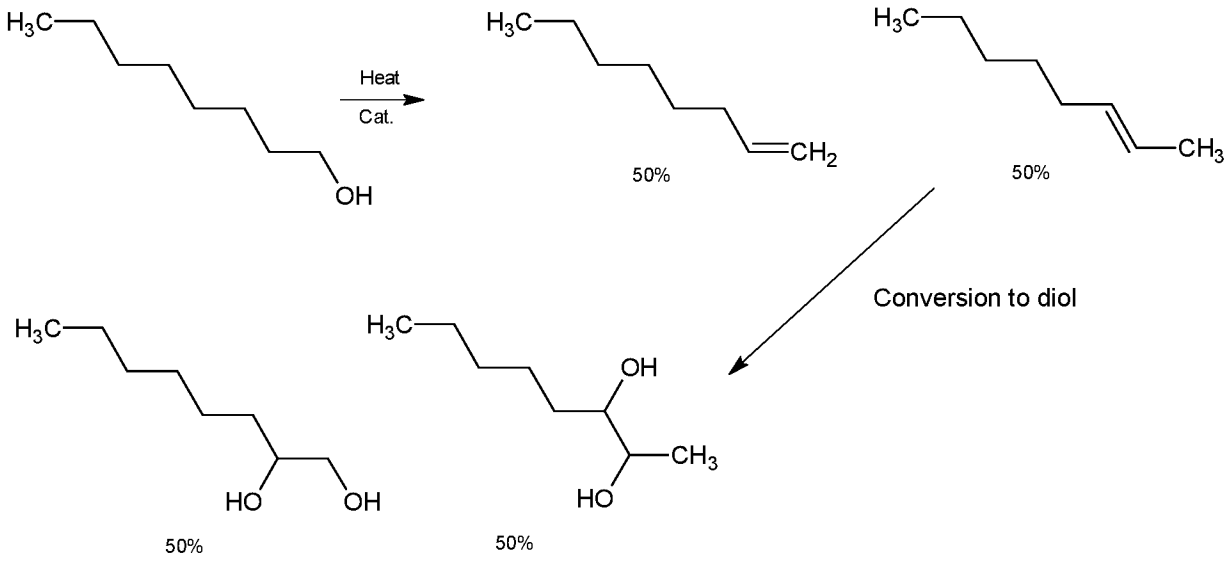


Table A

Catalyst	1-Octene (%)	2-Octene & 3-Octenes (%)	1-Octanol (%)	1-Octene Selectivity (%)
Alumina	87.7	5.3	4.7	94.3



As can be seen from the above-reaction schemes, the use of heat and a traditional acid catalyst converts 1-octanol to an alkene, *i.e.*, octene. Exposure to the acid sites in the catalyst allows the more thermodynamically stable 2-octene to form along with 1-octene. The 2-octene regioisomers formed (including 3-octene as shown above and 4-octene (not shown)) are very

difficult to separate from the 1-octene and afford a lower net chemical yield of the desired 1-octene. It follows that an increased or higher regioselectivity is a critical factor in the catalytic dehydration of 1-octanol to 1-octene and a desired goal to achieve in the relevant art. When using renewable and natural feedstocks, reaction efficiency (*i.e.*, chemical yield) of the desired product (*i.e.*, 1-alkenes) is critical. There remains a need in the art for a highly regioselective dehydration of 1-octanol that also has high chemical conversion using efficient process equipment and operating in a rapid and energy efficient manner.

[0021] Thus, traditional pathways using an octene mixture of regioisomers as shown above for conversion to a desired terminal 1,2-octanediol is reduced and the yield is also reduced. This makes the ability to form the desired alternative preservative materials chemically inefficient and not cost effective, creates more waste in process, and makes the overall process less sustainable. There is a strong need in the art for a highly regioselective, and high-chemical conversion rate process for creating a bio-1-octene from a bio-1-octanol.

[0022] International patent Publication No. WO 2004/078336 A2 uses a γ-alumina having no additional promoters but that was instead given a very large pore size and volume to enhance regioselectivity for dehydration of 1-octanol. In this work, the regioselectivity was high (97.7%), but, the chemical conversion was 65% and product selectivity for octenes was only 25%. Thus, the chemical yield of 1-octene from 1-octanol using this catalyst system was only about 15.9%.

[0023] In another example, U.S. Patent No. 7,576,250 B2, formation of 1-octene by cracking an ether derivative of 1-octanol is described. In this patent, the 1-octanol must first be converted to the methyl ether (*i.e.* methyl octyl ether) and then the ether is subjected to and passed over a γ-alumina catalyst. This involves extra chemical and added cost to make the ether and loss of the methanol in the process leading to a very ineffective and atom inefficient method. Most notably, the catalyst goes from having good conversion and regioselectivity in the first few hours, then, in just a mere 20 h of time-on-stream ("TOS"), all catalysts disclosed in the art show a constant and significant decrease in chemical conversion with a concomitant loss in regioselectivity. This type of short catalyst life time is not acceptable in commercial production efforts.

[0024] A lead-containing alumina catalyst is described in Chinese Patent No. 105312044 B, wherein plumbite pseudoboehmite showed high apparent selectivity and conversion. The catalyst had a carbon deposition rate of ~0.04%/h, which is highly undesirable and would be

unsatisfactory for something like 1000 h of continuous operation. Even more limiting is these catalysts incorporate a toxic heavy metal, namely lead. The use of these catalysts would require costly environmental controls and worker safety precautions if used on the industrial scale for commercial production

[0025] One path to making a "natural" alkanediol is by fermentation of biomass to form a straight chain, linear alkanediol. For example, U.S. Patent Application Publication No. 2005/0069997 A1 teaches formation of 1,3 propanediol from fermentation broth. However, 1,3-propanediol is not a 1,2-alkanediol. Fermentation processes that form long chain diols are chemically inefficient (*i.e.*, poor life-cycle-analysis numbers) and additionally require use of GMO-bacteria or -yeast, especially if one attempts to make a long carbon 1,2-alkandiol.

[0026] Another example of a natural bio-alcohol that is described in the art is bio-1-butanol, a known substance that has been used in commercial production since the discovery by Pasteur in 1862 of the acetone-butanol-ethanol fermentation process carried out by *clostridum* bacteria (a non-GMO bacteria), although it is used in very limited quantities currently. These bacteria ferment both C_5 and C_6 sugars to form a mixture of acetone, 1-butanol and ethanol (*i.e.*, ABE). Since the discovery of ABE, advances in fermentation processes can provide optimized production of bio-1-butanol over acetone and ethanol production. While the production is improved, it remains difficult and energy intensive to purify the bio-1-butanol from the fermentation broth and other impurities involved in the fermentation process such as ethanol and acetone. In addition, applicant is unaware of a non-GMO bacteria or yeast process that can form longer chain alcohols (*i.e.*, chains of six or more such as 1-hexanol or 1-octanol).

[0027] Bio-1-butanol is known as a source to make biofuels and provides a pathway for converting straight-chain, linear, primary four-carbon alcohols to bio-1-alkenes at very high yield to improve biofuel production and can also be used, for example in production of eco-friendly tires. In this method, bio-1-alcohols are dehydrated to bio-1-alkenes with high selectivity and chemical yield. The resulting bio-1-alkenes are useful in preparing high flashpoint diesel and jet biofuels useful for civilian and military applications. The bio-1-butanol is dehydrated using a solid phase dehydration catalyst that includes an inorganic support, such as γ-alumina or zinc aluminate ($ZnAl_2O_4$), and that has been treated/modified with a basic aqueous solution. The support may be further treated with an organosilane diluted in at least one hydrocarbon solvent. The process can convert bio-1-butanol from a fermentation

process that contains 0.1 to about 90 wt% water and produces a corresponding 1-alkene at a 92-99% regioselectivity, with only a single pass over the solid-phase catalyst, produing a reaction conversion of greater than 95% and a chemical yield of greater than 90% of the bio-1-butene. However, even with such a result for bio-1-butene, it is noted that the conversion of 1-octanol to 1-octene is not simply a homolog of a conversion of 1-butanol to bio-1-butene. In fact, comparative examples described herein below, illustrated that silanization of the catalyst leads to a *loss* of regioselectivity for the dehydration chemistry of 1-octanol.

[0028] Based on the foregoing, while progress has been made, there is a need in the art for continued improvement to consumer products such as personal care products, household products, industrial products and pharmaceutical products to provide additives, especially for antimicrobial use or for boosting the effects of known preservatives or alternative preservation systems, so as to keep products safe from contamination and fresh in storage and in use, while avoiding traditional preservatives and finding and relying on components for consumer product compositions from natural bio-sources. There is more particularly a need for a natural, and prefereably renewable/sustainable feedstock source to create a natural, bio-caprylyl glycol (*i.e.*, a natural or bio-1,2-octanediol) and the associated bio-1-alkene intermediate.

BRIEF SUMMARY OF THE INVENTION

[0029] The invention provides efficient pathways to achieve a 100% "natural" or "bio-compound" that is an authentic "natural" material, and preferably includes bio-1,2-alkanediols of carbon lengths from about 5 to about 20, and preferably from 5 to about 14, that can be used alone, in combinations of different types of bio-1,2-alkanediols, or in blends with other natural or traditional antimicrobials and other cosmetic additives.

[0030] The invention includes a process for the synthesis of bio-1,2-alkanediols, comprising: providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

[0031] In one embodiment of the process, the bio-alkene and the bio-1,2-alkanediol each have a carbon chain of about 6 to about 14 carbon atoms. The bio-alkene and the bio-1,2-alkanediol each may have a carbon chain length of about 6 to about 10 carbon atoms. The bio-alkene and the bio-1,2-alkanediol each may have a carbon chain length of about 6 to about 8

carbon atoms. For example, the bio-alkene may be bio-octene and the bio-1,2-alkane diol may be bio-1,2-octanediol.

[0032] In a further embodiment of the process, the bio-alkene preferably results from a process wherein a bio-1-alcohol is dehydrated by heating the bio-1-alcohol in a reactor with a catalyst. The reactor may be a fixed bed reactor. The fixed bed reactor may also be, *e.g.*, a fluidized fixed bed reactor. In such an embodiment, the catalyst may be selected from $ZnAl_2O_4$ and a γ-alumina catalyst.

[0033] The bio-alkene in a preferred embodiment has a bio-1-alkene regioselectivity of about 92% to about 99%, and preferably about 95% to about 99%. The process also preferably yields at least about 92% to about 99% of the bio-1,2-alkanediol.

[0034] As noted above in one embodiment a catalyst treatment may be used. The catalyst may be a γ-alumina catalyst treated with a base to form a modified γ-alumina catalyst. The base may comprise a Group I or a Group II metal. The γ-alumina catalyst may be treated, *e.g.*, with a calcium promoter to provide a modified γ-alumina catalyst. The modified γ-alumina catalyst may then be calcined to provide a calcined γ-alumina catalyst. In one embodiment, wherein a calcium promoter is used, the calcium promoter may be used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination, and preferably about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination.

[0035] A preferred temperature during calcination is about 400°C to about 500°C, more preferably about 420°C to about 480°C, and most preferably about 440°C to about 460°C. Calcination may be carried out in an oven. The calcination may be performed in air or under an atmosphere of nitrogen or other inert gas(es).

[0036] The bio-alkene preferably undergoes a distillation step to refine the bio-alkene prior to converting the bio-alkene to the bio-1,2-alkanediol. The bio-1,2-alkanediol formed from the bio-alkene may also undergo a final distillation step to refine the bio-1,2-alkanediol.

[0037] In another embodiment of the process, the bio-alkene may result from a process wherein the bio-1-alcohol in water is dehydrated by heating the bio-1-alcohol with a catalyst using no purge gas or under a purge gas. The purge gas may preferably be nitrogen but other inert gases may be used within the scope of the invention.

[0038] The bio-alkene in the process may also be converted to the bio-1,2-alkanediol by reacting the bio-alkene in the presence of at least one of peracid, *e.g.*, formic acid or acetic acid,

and hydrogen peroxide to form a mixture of bio-1,2-epoxyalkane having an epoxy ring and bio-1,2-alkanediol, and contacting this mixture with water and sodium hydroxide to complete formation to the bio-1,2-alkanediol.

[0039] The overall process preferably process yields at least about 60% to about 99% of the bio-1,2-alkanediol, and more preferably yields at least about 72% to about 99% of the bio-1,2-alkanediol.

[0040] The invention further includes a process for making bio-1,2-alkanediols, comprising: providing a bio-1-alcohol and a catalyst treated with a base; dehydrating the bio-1-alcohol in the presence of the catalyst to form a bioalkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms. Preferably, the catalyst is treated with a promoter and then calcined.

[0041] The catalyst in this process may also be a γ-alumina catalyst and the base may comprise calcium. The γ-alumina catalyst is preferably treated with a calcium promotor and after treatment is calcined at a temperature of about 400°C to about 500°C. The process preferably yields about 92% to about 99% of the bio-1,2-alkanediol.

[0042] The invention further includes a method for treating a catalyst for use in dehydration of alcohols, comprising providing a γ-alumina catalyst; treating the γ-alumina catalyst with a base, preferably a promoter as described herein, comprising a Group I or a Group II metal; and heating the γ-alumina catalyst to a temperature of about 400°C to about 500°C, which is preferably done in a very controlled and deliberate manner. The base may comprise calcium, and preferably the base may be a calcium promoter and the heating occur during calcination. The calcium promoter may be used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination, and more preferably in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination, preferably after careful calcination. The temperature during calcination in a preferred embodiment may be about 420°C to about 480°C, and more preferably may be about 440°C to about 460°C. Beneficial results are achieved based on the applicant's process including the preferred ranges noted. Applicant's determined that high calcination temperatures decrease catalyst regioselectivity and thus chemical yield of bio-1-alkene.

[0043] The invention further includes a composition, comprising at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

[0044] The composition may be a personal care composition, such as a hair care composition, an oral care composition, a skin care composition or a cosmetic composition.

[0045] The composition may also be a composition for a household product, such as a fabric care product or a cleaning product.

[0046] The composition may also be an industrial composition, or a pharmaceutical composition, a vitamin composition, or a health care composition.

[0047] In one embodiment of the composition herein, the composition may comprise a second bio-1,2-alkanediol, different than the first bio-1,2-alkanediol, the second bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a second bio-alkene, preferably regioselectively, such that the resulting bio-alkene of about 5 to about 20 carbon atoms has a terminal bio-alkene content of at least about 80% and a bio-1-alkene regioselectivity of at least about 80%. The composition may comprise at least one other bio-compound different from the first and the second bio-1,2-alkanediols. In another embodiment, the composition may comprise an antimicrobial compound different from the first and the second bio-1,2-alkanediol and different from the other bio-compound. The composition may also further comprise at least one other bio-compound different from the at least one bio-1,2-alkanediol, and in another embodiment, such a composition may also further comprise at least one antimicrobial compound different from the at least one bio-1,2-alkanediol and different from the other bio-compound. The first bio-1-alkene in such composition preferably has a regioselectivity of about 92% to about 99% and more preferably about 95% to about 99%. The first bio-alkene may be a bio-octene and the at least one first bio-1,2-alkane diol may be a bio-1,2-octanediol.

[0048] Also included in the invention is a method for providing an antimicrobial effect to a composition, including incorporating an antimicrobial system to the composition, wherein the antimicrobial system comprises at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of at least one first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. The antimicrobial system may further comprise a

second bio-1,2-alkanediol different than the first bio-1,2-alkanediol, wherein the first bio-1,2-alkanediol has a carbon chain length of about 5 to about 20 carbon atoms and is formed by regioselectively converting a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. The composition may further comprise at least one other bio-compound different from the first and the second bio-1,2-alkanediols, and in another embodiment may comprise at least one other preservative compound different from the first and the second bio-1,2-alkanediol and different from the other bio-compound. Such a composition may also further comprise at least one other bio-compound different from the at least one first bio-1,2-alkanediol. The antimicrobial may also further comprise at least one other antimicrobial compound and/or preservative compound different from the at least one first bio-1,2-alkanediol and different from the other bio-compound. The antimicrobial system may be made so as to demonstrate antimicrobial efficacy. The first bio-1-alkene preferably has a regioselectivity of about 92% to about 99%, and preferably about 95% to about 99%. The first bio-alkene may be bio-octene and the at least one first 1,2-alkane diol may be a bio-1,2-octanediol.

[0049] The invention further includes in one embodiment a method for boosting the antimicrobial efficiency of an antimicrobial and/or a preservative in a composition, comprising incorporating an antimicrobial system into the composition, wherein the second antimicrobial system comprises at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by regioselective conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. In the method, the antimicrobial system may further comprise a second bio-1,2-alkanediol different than the first bio-1,2-alkanediol, wherein the second bio-1,2-alkanediol has a carbon chain length of about 5 to about 20 carbon atoms and is formed by conversion of a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. In the composition, it may further comprise at least one other bio-compound different from the antimicrobial and/or preservative and different from the first and the second bio-1,2-alkanediols. The composition may also further comprise at least one other bio-compound different from the at least one first bio-1,2-alkanediol. The first bio-1-alkene preferably has a regioselectivity of about 92% to about 99%., and more preferably about 95% to about 99%. In one embodiment, the antimicrobial system demonstrates antimicrobial efficacy. The first bio-

alkene may be a bio-octene and the at least one first bio-1,2-alkane diol may be a bio-1,2-octanediol.

[0050] In yet a further embodiment, the invention includes an antimicrobial product, comprising at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. The product may further comprise a second bio-1,2-alkanediol, different than the at least one first bio-1,2-alkanediol, the second bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms and formed by conversion of a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

[0051] The antimicrobial product may further comprise at least one other bio-compound different from the at least one first and the second bio-1,2-alkanediols. In one embodiment, the product may further comprise a second antimicrobial and/or a preservative different from the antimicrobial product. The product may also further comprise at least one other bio-compound different from the at least one first bio-1,2-alkanediol, and may also further comprise a second antimicrobial and/or a preservative different from the antimicrobial product. The first bio-1-alkene preferably has a regioselectivity of about 92% to about 99%.

[0052] The antimicrobial product preferably also demonstrates antimicrobial efficacy. The first bio-alkene may be bio-octene and the at least one first 1,2-alkane diol may be a bio-1,2-octanediol.

[0053] The invention also includes a product for boosting the efficacy of an antimicrobial and/or a preservative in a composition, the product comprising at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. Such product may further comprise a second bio-1,2-alkanediol, different than the at least one first bio-1,2-alkanediol, the second bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms and formed by conversion of a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%. The composition of the product may also further comprise at least one other bio-compound different from the at least one first and the second

bio-1,2-alkanediols, and also may further comprise at least one other bio-compound different from the at least one first bio-1,2-alkanediol. The first bio-1-alkene preferably has a regioselectivity of about 92% to about 99%. The first bio-alkene may be bio-octene and the at least one first bio-1,2-alkane diol may be bio-1,2-octanediol. The product preferably demonstrates antimicrobial efficacy.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0054] The foregoing summary, as well as the following detailed description of preferred embodiments of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there is shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0055] Fig. 1 is a process flow chart of steps in a preferred embodiment of a process described herein;

[0056] Fig. 2 is graphical representation of $\delta^{2}H$ and $\delta^{13}C$ values for petroleum-based alcohols, alkenes and acids and the corresponding natural and renewable analogs;

[0057] Fig. 3 is the Gas Chromatograph (GC) chromatogram of the reactor output from the dehydration of bio-1-octanol using the catalyst prepared in Example 4 at 0.2ml of bio-1-octanol feed and heated to 315°C;

[0058] Fig. 4 is the GC chromatogram of the bio-1-octene obtained from the reactor after distillation;

[0059] Fig. 5 is the GC chromatogram of the bio-1,2-octanediol obtained from dehydration of bio-1-octene, conversion to the 1,2-octanediol and then fractional distillation of the 1,2-octanediol;

[0060] Fig. 6 is the GC chromatogram of the petro-1,2-octanediol currently approved for use in cosmetic formulation; and

[0061] Fig. 7 is a photo comparing catalyst with 1400 h TOS (left) and new catalyst (on right).

DETAILED DESCRIPTION OF THE INVENTION

[0062] The invention includes a process for the synthesis of bio-1,2-alkanediols. As used herein, "bio" when used with "alkanediol," or any specific alkanediol compounds noted within this class of compounds is intended to mean as described above that the compound, and preferably all of the carbons in the compound within this class of compounds, as described further below are "natural" compounds that are also authentic natural compounds derived from plant sources (algae-, plant-, animal- or biomass-derived) and are non-petrochemically derived (*i.e.*, not derived from a non-renewable resource such as fossil fuel, petroleum or other "old" carbon source). In this sense, as they are derived from renewable materials, they are also sustainable compounds. It also means that such materials are formed from bio-alkenes. When used in the terms, "bio-alcohol," or "bio-alkene," and similar compounds herein, "bio" is intended also to have the same connotation as noted above for describing "bio-1,2-alkanediol." Such materials should preferably satisfy the requirements of having and being derived from an authentic or "new" carbon material (non-petrochemically derived) feedstock as confirmable through testing such a compound using mass spectroscopy as described above and/or gas chromatography, the current ASTM D6866-16 standard or prior methods such as specific stable isotope analysis (CSIA). The invention further includes the bio-1-alkenes and bio-1,2-alkanediols resulting from the synthesis process, as well as various products incorporating them. The invention further includes a method for treating a catalyst, which may be used in embodiments herein for dehydrating a bio-1-alcohol to form a bio-alkenes used in the processes herein for forming bio-1,2-alkanediols.

[0063] The invention provides efficient pathways to 100% "natural" or "bio" compounds that are from new carbon or authentic carbon materials that are not petrochemically derived and are preferably used in compositions and products that can be made for a wide variety of end uses and compositions, including as components of antimicrobial compositions and as cosmetic additives, among other uses described herein.

[0064] Also disclosed herein are methods of using bio-1,2-alkanediols for use as antimicrobials in a composition such as in or with an alternative preservation system and/or as hurdle technology. Also disclosed are various compositions comprising bio-1,2-alkanediols, including when used as an antimicrobial Also described are methods of boosting the antimicrobial efficacy of a composition already including a preservative or alternative

preservation system, and the resulting boosted antimicrobial efficacy composition. Each of such methods includes incorporating into the composition a bio-1,2-alkanediol, combination(s) of at least two different bio-1,2-alkanediols, or combination(s) of at least one bio-1,2-alkanediol with at least one other bio-compound different from the at least one bio-1,2-alkanediol, wherein the bio-1,2-alkanediol(s) either act as a antimicrobial or boost the efficacy of another antimicrobial, preservative or other alternative preservation system already present in a composition. The bio-1,2-alkanediols may themselves be an antimicrobial product and/or a antimicrobial efficacy boosting product whether used alone, in combinations of one or more different bio-1,2-alkanediols, or in combination(s) of one or more different bio-1,2-alkanediols with at least one other bio-compound different from the bio-1,2-alkanediols and/or an optional, different antimicrobial, preservative or alternative preservation system. The bio-1,2-alkanediols when used in compositions herein exhibit antimicrobial efficacy.

[0065] In one embodiment herein, a process is described herein for synthesis of bio-1,2-alkanediols. As noted above, materials referred to herein as "natural" are intended to include materials that are non-petrochemically derived and are sustainable, whether synthesized from non-petrochemically derived, natural materials or formed from a natural, and preferably an authentic natural or bio-based source.

[0066] The method includes providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms, preferably about 6 to about 14 carbon atoms, and more preferably about 6 to about 10 carbon atoms, with a bio-1-octene being preferred. The bio-alkene is preferably a bio-1-alkene with a traditional α-olefinic structure. It also preferably has a regioselectivity when prepared of at least about 80%, more preferably at least about 92% and most preferably at least about 95% up to as much as 99%.

[0067] Such bio-alkenes may be bio-1-pentene, bio-1-iso-pentene, bio-1-hexene, bio-1-heptene, bio-1-octene, bio-1-nonene, bio-1-decene, bio-1-dodecene, and related bio-1-alkenes up to chain length of 20 carbons. Larger or smaller bio-alkenes may also be made, however, the preferred bio-alkenes for use herein are those with sufficient chain length to serve as effective antimicrobials when converted to bio-1,2-alkanediols without losing the desired properties. Such bio-alkenes may be straight or branched chain molecules, although straight chain molecules are preferred and may include one or more functional or substituted groups for desired end effects in the end use application, for example, sulfonate groups, hydroxyl groups, ether groups, amide groups, carbonyl groups, carboxylic acid groups, amine groups, fluorinated

groups, aryl or arene groups, and similar functional groups without intending to be limiting. Preferably any such functional or substituted groups do not interfere with conversion to an alkanediol or with the antimicrobial end application desired for the particular alkanediol.

[0068] Such bio-alkenes, such as bio-1-hexene and bio-1-octene, as are generated according to the invention, may be used to make bio-1,2-alkanediols as described herein, and may also be used to make other bio-based compounds and polymers, including, *e.g.*, for synthesis of bio-based olefin copolymers. Bio-1-alkenes herein may be used, for example, in free radical or catalytic polymerization processes as are known in the art, to yield a variety of bio-polyalphaolefins homopolymers and copolymers, which are useful as lubricants and cosmetic ingredients. A further example, includes bio-linear low-density polyethylene (bio-LLDPE) can be prepared via copolymerization of bio-ethylene (derived via dehydration of sugarcane derived bio-ethanol to bio-ethylene) with bio-1-alkene copolymers yielding 100% renewable bio-LLDPE, a thermoplastic resin useful in film applications such as food and non-food packaging and shrink/stretch films.

[0069] The process of the invention includes an embodiment wherein the process makes bio-1,2-alkanediols, including providing a bio-1-alcohol and a catalyst treated with a base, preferably with a promoter and then calcined; dehydrating the bio-1-alcohol in the presence of the catalyst to form a bioalkene having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

[0070] An overall flow diagram of a preferred process of making bio-1,2-alkanediols, that incorporates a preferred method of treating a catalyst as described further below is provided as embodiment 100 as shown in Fig. 1.

[0071] In the process generally referred to herein as process 100, in Fig. 1, prior to introducing the bio-1-alcohol, a catalyst is prepared. A suitable γ-alumina catalyst, e.g., Al_2O_3, 110 is introduced into a reactor 101 into which a calcium promotor or other base treatment material 102 as described further below is introduced. After a suitable treatment described in detail below, a modified catalyst 103 leaves reactor 101 and enters a heated chamber 104 such as an oven for heat treatment. If a catalyst promoter is used, for example, a calcination step occurs at preferred and controlled temperature ranges to increate a level of regioselectivity in a resulting bio-alkene in the next step. After, e.g., calcination in chamber 104, the calcined or otherwise heat-treated catalyst 105 is introduced along with a bio-1-alcohol 106 such as bio-1-

hexanol or bio-1-octanol into a reactor 107 to promote intimate contact between the alcohol and the catalyst. Suitable reactors included fixed bed reactors, fluidized bed reactors, tubular reactors, and other suitable reactors. After sufficient time for dehydration of the bio-1-alcohol to a bio-alkene 109, which highly regioselects to a bio-1-alkene, a further, optional distillation or other purification or refining step in a column(s) or other equipment 110, may occur. The refined or otherwise purified and highly regioselective bio-alkene, which should be of a high quantity of bio-1-alkene, is then introduced to a reactor 112 in order to convert the bio-1-alkene into a bio-1,2-alkane diol 113. Such bio-1.2-alkane diol 113 may be further and optionally refined such as by distillation in a column(s) or through other steps in equipment 114. After purification or distillation, a final high yield of up to 99% is removed as the final bio-1,2-alkane diol 115.

[0072] The bio-1-alkene may be made using a catalytic process, and preferably using a catalyst that has been treated according to the method described herein. In one embodiment, the bio-alkene, which is preferably made herein to be of a high regioselectivity bio-1-alkene is formed using a bio-1-alcohol that is dehydrated by heating the bio-1-alcohol in the presence of a catalyst. This may be done, for example, by passing the bio-1-alcohol through a fixed bed reactor, or a fluidized bed reactor. The fixed bed may be packed with a catalyst, preferable a treated catalyst having been treated using techniques as described below.

[0073] For example, a bio-1-alcohol derived from a plant source, including biomass that can produce a related acid (*e.g.*, 1-octanol may be derived from coconut, palm or other plant source or biomass that can produce octanoic acid, which is subsequently reduced via catalytic dehydrogenation to 1-octanol). The bio-1-alcohol is then dehydrated regioselectively by feeding the material at an elevated temperature into, *e.g.*, a fixed bed reactor or other suitable reactor providing intimate contact between the bio-1-alcohol and the catalyst. The fixed bed may be packed with or otherwise arranged to provide sufficient contact with a catalyst. Other suitable reactors may be provided for this purpose provided they can achieve suitable contact for assisting in dehydration. Examples include tubular reactors, fixed and fluidized bed reactors, and the like.

[0074] The reactor can be designed as a simple heated reaction tube packed with catalyst and a flow of the gaseous bio-1-alcohol over the catalyst, preferably in a single pass affording greater than about 95% conversion, with greater than about 98% a preferred embodiment, and in all cases with no recycle stream used whatsoever in the overall process flow. In one

embodiment, the reaction tube is heated isothermally, the tube having from 1 to 10 reaction zone temperatures along the length of the tube, each heated in the range of about 240°C to about 360°C in order to optimize catalyst performance. In a preferred embodiment, the reaction tube has 1 to 4 reaction zone temperatures in the range of about 260°C to about 340°C.

[0075] In one embodiment the process is carried out in a fluidized bed reactor operated in the temperature range of about 240°C to about 360°C. Other continuous flow reactor designs can be used in accordance with procedures and practices used by those familiar with the art of chemical engineering.

[0076] The catalyst used may be prepared by treating γ-alumina (*e.g.*, Porocel® CatGuard®) with at least one base, preferably a promoter, such as with sodium hydroxide, potassium hydroxide, calcium acetate and the like to create a second catalyst. This second catalyst is then calcined to create a third catalyst. The calcination temperature has been found to be most unexpected and critical to creating the most effective catalyst. As seen below when calcined at about 500°C, a significant drop occurs in regioselectivity compared to catalysts calcined at lower temperatures. In one embodiment, as demonstrated in Table 1 below, preferred calcination temperature is about 400°C to about 480°C, and a more preferred calcination temperature is about 440°C to 460°C.

Table 1

Catalyst	Calcination Temperature (°C)	1-Octene (%)	2-Octene & 3-Octenes (%)	1-Octanol (%)	1-Octene Selectivity (%)
EXAMPLE 1	440	94.0	3.2	1.6	97.4
EXAMPLE 2	500	88.9	6.6	3.5	93.1

[0077] Varying catalysts may be used for assisting the bio-1-alcohol in the dehydration step. However, it is preferred that a suitable catalyst that can achieve high levels as regioselectivity as described herein is used. Suitable catalysts include γ- alumina-based catalysts and $ZnAl_2O_4$. Preferably, the catalyst is treated with a base, such as with sodium hydroxide, potassium hydroxide, calcium acetate and the like. In one preferred example, the catalyst is a γ-alumina catalyst treated with a base including a Group I or Group II metal. In

one more preferred embodiment, calcium may be included in the base, and a calcium promoter used. After being treated with the calcium promoter to form a modified γ-alumina catalyst, in a further preferred embodiment, the modified γ-alumina catalyst is then calcined using varying calcination techniques but at temperatures which are preferably much lower than used in standard calcination methods to provide a calcined γ-alumina catalyst. The initial treatment provides a modified γ-alumina catalyst that is then calcined to be ready for use for varying processes including in the dehydration step of the processes herein for making bio-1-alkenes and their subsequent conversion to bio-1,2-alkandiols.

[0078] When employing a calcium promoter, it may be used in the treatment noted above in amounts of about 0.01 weight percent to about 4 weight percent, based on the amount of CaO determined after calcination. In preferred embodiments, about 1 weight percent to about 2 weight percent of the calcium promoter is used based on the amount of CaO determined after calcination.

[0079] In another embodiment, if desired, the alumina-based treated catalyst may be further organosilanized with an organosilane by treatment with, for example, diethoxydiphenylsilane to form an organosilanized base-treated γ-alumina catalyst. The organosilanzized base may be, for example, diethoxydiphenylsilane, dichlorodiphenylsilane and similar materials.

[0080] In one embodiment a catalyst support may comprise $ZnAl_2O_4$ and may also be modified by a base, e.g., by reaction with a promoter and similar catalysts and modified catalyst materials known or to be developed that are capable of carrying out the process as noted herein in a manner similar to the catalysts noted herein that can create a high level of regioselectivity could also be used.

[0081] The catalysts as noted above in addition to being suitable if treated with a base, may alternatively or also be treated with an organosilane or organosilane-modified material to create a promoter-modified catalyst. This promoted catalyst may be further organosilanized with an organosilane by treatment with diethoxydiphenylsilane to create a third, organosilanized and promoter-modified γ-alumina catalyst. The organosilane used to modify the catalyst may be, for example, diethoxydiphenylsilane, dichlorodiphenylsilane and similar materials. As seen in EXAMPLE 10 herein, silanization of the catalyst leads to a decrease in bio-1-octene selectivity, once again showing a difference from previous art and the direct and proven differences in the dehydration catalyst makeup necessary for a highly regioselective dehydration of 1-butanol or 1-octanol.

[0082] In other treatment techniques herein, the γ-alumina catalyst may be modified by the technique of incipient wetting impregnation. A solution of the base is used to modify a solid support in a manner so as to avoid excess moisture that can result in support damage and chemical change. In one embodiment, the incipient wetting impregnation solution (IWS) is about 40% to about 100% the weight of the solid support, which may be, for example an untreated γ-alumina catalyst. In one embodiment, the untreated γ-alumina catalyst is selected from the commercially available, Porocel® CatGuard®. Preferably, the IWS is about 50% to about 60% of the catalyst support weight.

[0083] The γ-alumina may also be provided in a powder form having a surface area of about 50 to about 400 m^2/g. The γ-alumina in one embodiment is shaped by a suitable extrusion process, as are known to those skilled in this art of solid phase catalysts. In one example, the γ-alumina is in the form of 1/16" to 1/8" cylindrical rods with a length to diameter ratio of about 20:1, preferably about a ratio of about 5:1. The extrudate can be in the shape of spheres, star-shaped, hollow cylinders or any three-dimensional shape that can ultimately deliver a γ-alumina with sufficient surface area pore volume, mechanical strength, and physical size to be used in a continuous flow reactor system.

[0084] Once prepared, *e.g.*, a base-treated, preferably a promoter treated, γ-alumina catalyst, as noted above is preferably calcined with care taken in regulating the temperature. This is done at an elevated temperature, preferably in a suitable chamber such as an oven, and the temperature range, while elevated to heat the materials, is not as high as calcination treatments typically used in prior catalyst processes. Instead, the temperature for calcination is kept at about 400°C to about 500°C, and preferably about 420°C to about 480°C, and most preferably about 440°C to about 460°C. Typically, prior standard calcination treatments occur at temperatures 500°C or higher with no limits established or specified for effectiveness. However, applicants discovered that by controlling this temperature and in the specific catalyst treatment process noted herein, the regioselectivity can be unexpectedly controlled to disproportionately favor formation of the bio-1-alkene when the bio-1-alcohol is dehydrated using the resulting calcined catalyst derived from a combination of catalyst treatment and a carefully controlled calcination process.

[0085] In the dehydration step herein, the bio-1-alcohol may be fed to a reactor undiluted or in water through the reactor. Optional an inert gas (*e.g.*, nitrogen) may be used as a purge gas to retain consistency and avoid contaminates in the process. The bio-1-alcohol is preferably

fed, such as by a pump (such as an HPLC pump) or pressurized gas source at a temperature of about 200°C to about 400°C, although temperatures may be adjusted for different bio-1-alcohols depending on the reaction time and flow rate, the catalyst selected and the desired outcome. As the product is removed from the reactor, it is preferably monitored to determine content, identification of product and the ratio of bio-1-alkene conversion as well as the regioselectivity. In a preferred embodiment, the bio-1-alkene has a regioselectivity of at least about 80%, and more preferably about 92% to about 99% and even more preferably about 95% to about 99%.

[0086] In one embodiment, the dehydration process as described in Fig. 1 using the invention catalyst, i.e., the catalyst resulting from the preferred treatment and calcination process noted above, can be stopped and the catalyst maintained under inert gas flow for extended periods of time. This shutdown period can be hours, days or weeks, with heating or no heating applied during this period. The invention catalyst can be re-heated and dehydration process resumed without any detrimental effect on catalyst activity or regioselectivity. Thus, the invention catalysts are not only robust in continuous operation, but they can withstand periods of rest (inactivity) without negative effect on catalyst performance when brought back on line.

[0087] The bio-1-alkene may also be formed using a process in which the bio-1-alcohol in water is dehydrated by heating the bio-1-alcohol with a catalyst under a purge gas as noted above in a bulk process or other continuous reactor. Base and optional organosilane treatments may also be used as well as catalysts and reaction conditions such as those noted above, and most preferably, through use of a calcined γ-alumina catalyst formed by the process described above.

[0088] The bio-1-alcohol may also be formed using a process in which the bio-1-alcohol in water is dehydrated by heating the bio-1-alcohol with a catalyst under a purge, but as noted above, in bulk process or some other continuous reactor. Base and optional organosilane treatments may also be used as well as catalysts and reaction conditions as noted above.

[0089] Once the bio-1-alcohol is dehydrated to form the highly regioselective terminal, bio-1-alkene, that material is then converted to a bio-1,2-alkandiol having a carbon chain length of about 5 to about 20 carbon atoms. Prior to conversion, the bio-1-alkene may optionally be further refined such as by a distillation, vacuum distillation, fractionation or similar refining step to further purify the bio-alkenes to remove trace impurities and minor undesired fractions.

For example, in forming a bio-1-octene, a C8 olefin content of about 90 weight percent to about 99 weight percent can be achieved, and at least about 95 weight percent and preferably about 97 weight percent or greater C8 olefin in the form of the *n*-α-olefin (*i.e.*, 1-octene) can be achieved. In addition, in forming a bio-1-hexene, a C6 content of about 95 weight percent to about 99.8 weight percent can be achieved, with at least about 96 weight percent to about 99 weight percent thereof having a 1-hexene structure.

[0090] Various chemical reactions may be used for this conversion as are known for use in standard alkene to alkanediol conversions using petrochemically derived starting materials and/or that are used for smaller chain bio-alkanes. For example, the bio-1-alkene is reacted in the presence of at least one of formic acid or acetic acid, and a peroxide such as hydrogen peroxide to form an intermediate solution including a bio-1,2-epoxyalkane, bio-1,2-alkanediol, and other components. This is then further contacted with a base solution, such as a sodium hydroxide or another suitable base solution, to complete formation of the bio-1,2-alkanediol. The process noted above preferably yields about 60% to about 99%, and more preferably about 70% to about 99% or about 75% to about 99% of bio-1,2-alkanediol.

[0091] A bio-1-alkanol may also be converted to bio-1-alkene for use in this process by dehydrating the bio-1-alkanol using heat and an acid catalyst in accordance with other previous techniques.

[0092] Bio-1,2-alkanediols, having a chain length of about 5 to about 20 carbon atoms and synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%, more preferably 92% to about 99% and most preferably about 95% to about 99%. In one embodiment, a bio-1-alkanol having a carbon chain of about 5 to about 20 carbon atoms is preferably first converted to a bio-alkene regioselectively such that the resulting bio-alkene contains a bio-1-alkene content of at least about 80% or higher as noted above. Then the bio-1-alkene is converted to the 1,2-alkanediol by any known method known in the art. The resulting bio-1,2-alkanediol after conversion may be further refined such as by distillation, vacuum distillation, fractionation or other similar steps as are noted above for refining the bio-1-alkene to provide a refined, final bio-1,2-alkanediol.

[0093] Resulting bio-1,2-alkanediols, having a chain length of about 5 to about 20 carbon atoms are preferably synthesized by first deyhydrating a bio-1-alkanol having a carbon chain of about 5 to about 20 carbon atoms to a bio-1-alkene having a regioselectivity of at least about

80%, more preferably about 92% to about 99% and most preferably about 95% to about 99% of bio-1-alkene is formed, then treating the bio-1-alkene with formic or acetic acid in the presence of hydrogen peroxide, and further with an aqueous base solution. The bio-1,2-alkanediol may then be separated from the aqueous solution by any suitable technique known in the art of making dihydroxyalkanes in general, and more specifically 1,2-alkanediols. In a preferred embodiment, a distillation step is included for this purpose.

[0094] The bio-1,2-alkanediols as described above, may be used in a variety of compositions, whether used alone or in combination with other different bio-1,2-alkandiols according to the present invention. Such compositions may incorporate one, two or more different bio-1,2-alkanediols according to the invention herein that may act within an antimicrobial system. Such bio-1,2-alkanediol(s), may be used alone as an antimicrobial additive or in an antimicrobial system incorporating other bio-compounds (*i.e.*, any suitable naturally derived, and preferably authentic natural product as tested using mass spectroscopy, gas chromatography and/or the ASTM standard noted above) such as bio-organic acids, bio-diols such as 1,3-propanediol, bio-1,2-butanediol, and 1,2-pentanediol that are extracts from fermentation products of bio-based starting materials and/or other antimicrobial materials, alternative preservatives, traditional preservatives or hurdle technology components as are known in the art or to be developed. An example of a preferred source of bio-compounds for use within the scope of the invention are trigylcerides. In yet a further example, another chemical group of bio-compounds that can be used in preparing alternative preservatives is commonly described as terpenoids. These natural terpenoids can have from 5 to 20 carbon atoms and can be readily obtained through sustainable farming practices, and may be used within the scope of "bio-compounds" as that term is used herein for us in combination with the bio-1,2-alkanediols herein.

[0095] When used in a composition, the bio-1,2-alkanediols of the invention are preferably incorporated in an amount of about 0.1 to about 10 weight percent, and preferably 0.3 to about 2 weight percent, of the total composition; which amount may be varied depending on whether they are used alone for antimicrobial effect or with other components in an antimicrobial system. In the latter instance, the bio-1,2-alkanediols are preferably present in a ratio of the bio-1,2, alkanediol(s) to any other antimicrobial component(s) of about 99:1 to about 1:99, and preferably about 75:25 to about 25:75 in the antimicrobial system (wherein the system would

include the bio-1,2-alkanediol(s) herein and/or any other antimicrobial, traditional preservative, alternative preservation and/or hurdle technology component(s) in the composition).

[0096] When used in certain compositions that are themselves viewed as "antimicrobial products" for providing to other formulators in various industries, the 1,2-bio-alkanediol(s) of the invention may be prepared initially as antimicrobial products that include one or more of the 1,2-bio-alkanediol materials made in accordance with the invention as described above and that incorporate one or more of the compositions as noted above, wherein such antimicrobial products may include also other bio-compounds, known antimicrobials, preservatives, alternative preservation materials or hurdle technology materials.

[0097] Examples of known preservatives and alternative preservative materials or compounds used in alternative preservation systems that may be used with the bio-1,2-alkanediols of the invention, include those suitable for use by various industries in which the present invention may be beneficial. For example, in the cosmetic and personal care industry, the bio-1,2-alkanediol(s) formed according to the present invention can be used alone, in combinations of two or more such materials and/or with other biocompounds and/or with known cosmetic preservatives and alternative preservation materials and/or hurdle technology components. Examples of preservative materials are listed by the FDA in the U.S. as including: (i) traditional preservatives, such as parabens (methyl, ethyl, propyl, and butyl), Quaternium 15 (aka "Dowicil"), diazolidinyl urea, imidazolidinyl urea, DMDM hydantoin, 2-bromo-2-nitropropane-1,3-diol (aka "Bronopol"), sodium hydroxyglycinate, phenoxyethanol, sorbic acid, potassium sorbate, methylisothiazolinone (aka "MI"), methylchloroisothiazoline (aka "CMI" often in combination with MI as Kathon CG), sodium benzoate, caprylyl glycol, sodium dehydroacetate, and formaldehyde; (ii) non-traditional or alternative preservatives: such as extracts of botanicals, organic acids, alcohols and glycerols, fermentation products, glyceryl caprylate, levulinic acid, p-anisic acid, eucalyptus globulus, glycyrrhiza, glabra (licorice) root extract, salvia officinalis, citrus grandis (organic grapefruit) extract, arnica montana (organic arnica) extract, boraxitrus seed extracts, leuconostoc/radish root ferment filtrate. goldseal (hydrastis canadensis root extract), citrus medica, limonum (Lemon) peel extract, caprylhydroxamic acid; and (iii) so-called "self-preserving" materials such as ethanol (when present at > 15%), butylene glycol (when present at >10%), propylene glycol (when present at > 20%); as well as (iv) other components used in alternative or traditional preservation systems in cosmetics such as MDM hydantoin, sodium hydroxymethylglycinate, benzisothiazolinone,

benzyl alcohol, dehydroacetic acid, benzoic acid, salicylic acid, iodopropynyl butylcarbamate chloroxylenol, methyldibromo glutaronitrile, chlorphenesin, triclosan, benzalkonium chloride, chlorhexidine, polyaminopropyl biguanide, 5-bromo-5-nitro-1,3-dioxane (bronidox), hexamidine diisethionate, pentylene glycol, ethylhexylglycerin, triclocarban, glyceryl caprylate, o-cymen-5-ol, chlorphenesin, and glyceryl monolaurate, and traditional petrochemically-derived 1,2-alkanediols such as 1,2-hexanediol, 1,2-octanediol.

[0098] Other countries have similar lists with variations on the nature and type of preservatives, alternative preservatives or preservative system or hurdle technology additives that may be used in those countries. However, the present bio-1,2-alkanediols may be used in such other materials as well. In each of the above-noted systems and compositions, the preferred bio-alkene used in the invention is a bio-octene and the at least one first bio-1,2-alkanediol is bio-1,2-octanediol.

[0099] Examples of compositions that may benefit from an antimicrobial system incorporating one or more of the bio-1,2-alkanediols formed according to the process noted above and/or in compositions as noted above include personal care compositions, such as hair care, oral care, skin care or cosmetic compositions; household product compositions, such as fabric care or cleaning products; industrial compositions; and pharmaceutical, vitamin, nutraceutical or other health care compositions, any of which could benefit from an antimicrobial system, component or antimicrobial product derived from an authentic, natural, bio-based material.

[0100] The bio-1,2-alkanediols are preferably incorporated into a cosmetic or personal care composition (on a wet-basis or total weight basis) so as to make up about 0.001% by weight to about 25% by weight of the composition, and more preferably about 0.01% by weight to about 10% by weight of the composition. The amount used may vary depending on whether other hurdle technology components or other preservatives are also being used in the composition.

[0101] Such bio-1,2-alkanediols alone, in combinations of two or more different bio-1,2-alkandiols, and/or in antimicrobial systems incorporating the bio-1,2-alkanediol(s) alone or with other bio-compounds and/or other preservative, alternative preservative or hurdle technology components, may also be used in a method to provide an antimicrobial effect to a composition, wherein the compositions may be any of the variety of types of compositions as noted above. It is preferred that the bio-1,2-alkanediols herein provide an antimicrobial effect and efficacy to a composition into which the bio-1,2-alkanediols are incorporated, whether into

a personal care, household, industrial, pharmaceutical, vitamin, nutraceutical or other health care composition. Such an antimicrobial effect may be demonstrated by using a variety of suitable antimicrobial effectiveness tests (AET). Such tests include, for example, a compendial test performed during formulation development and stability testing in parenteral drug products intended as a multi-dose product. Suitable test procedures and acceptance criteria are described in the *U.S. Pharmacopeia*, AET, the *European Pharmacopeia* (Efficacy of Antimicrobial Preservation), and the *Japanese Pharmacopeia* (Preservation Effectiveness Tests). Other suitable challenge tests may be used. The FDA also recommends suitable challenge testing.

[0102] One group of antimicrobials, some of which are in the group noted above, are other alcohols, and preferably at least one other alcohol, preferably at least one other diol, and most preferably one or more other vicinal diols that may be petrochemically derived, albeit, it is preferred that such materials are used a diluents or in smaller amounts for providing some antimicrobial effect, but are not so great as to diminish the impact of the natural, bio-based 1,2-alkane diols of the present invention. By the term, "vicinal diols," it is meant materials that have hydroxyl groups which are bonded to atoms in the molecule which are next to each other, *i.e.*, wherein two atoms each bearing a hydroxyl group are bonded to each other. Examples of vicinal diol compounds suitable for use in the invention, include, but are not limited to, ethylene glycol and propylene glycol. Such materials are used in the personal care, cosmetic and pharmaceutical arts as humectants and solvents, and as described in U.S. Publication No. 2007-0207105-A1 as having some modest antimicrobial activity.

[0103] Preferred vicinal diols for use with the bio-1,2-alkanediols herein, in compositions described for use in personal care and pharmaceutical use compositions are medium-chain length, linear vicinal diols that demonstrate some antimicrobial activity including petrochemically-derived 1,2-pentanediol, 1,2-hexanediol, 1,2-octanediol, and 1,2-decanediol. Other vicinal diols useful in the compositions described herein include molecules derived from glycerin. Glycerin can be reacted with other molecules at its 1- or 3-position, leaving two vicinal hydroxyl groups. For example, glyceryl monoethers, such as ethylhexylglycerin [3-(2-ethylhexyloxy)propane-1,2-diol], available commercially as SENSIVA®SC50 from Schulke & Mayr, are useful, traditional, liquid vicinal diols having antimicrobial properties. Glyceryl monoesters such as glyceryl monolaurate, glyceryl mono caproate, or glyceryl monocaprylate, the latter of which is commercially available from Inolex Chemical Company, Philadelphia, PA, are also useful antimicrobial vicinal diols. For the preservation of cosmetics, toiletries and

pharmaceuticals, vicinal diols are known to be effective against bacteria and yeast but weak against fungi and to date there are only limited natural choices, none of which to applicant's knowledge are bio-derived natural 1,2-alkanediols of from 5 to 20 carbon atoms.

[0104] The compositions herein preferably do not include, or include only to a minor amount any preservation materials such as parabens, or other known preservation materials that can be viewed as harmful to the user.

[0105] Such personal care and pharmaceutical compositions may optionally further include a solubilizing agent in amounts of about 1% to about 70% by weight of the combination of the solubilizing material with the bio-1,2-alkane diol(s) (or if used with other preservation component(s) by weight of the entire antimicrobial system with the solubilizing material). Suitable solubilizing agents include vicinal and other traditional diols.

[0106] Also useful in with the bio-1,2-alkanediols in any antimicrobial system are hydroxamic acid and the like which may be used in a variety of industries. Suitable hydroxamic acids include alkylhydroxamic acids and bio-alkylhydroxamic acids that include at least one alkyl group of a chain length of about two to about twenty-two carbon atoms, which may be branched or linear in structure, substituted or unsubstituted, and saturated or unsaturated as noted hereinabove. Preferred alkylhydroxamic acids contain alkyl groups of a chain length of about six to about twelve carbon atoms and most preferably linear chains of that length. Most preferred alkylhydroxamic acids are caprylohydroxamic acid, having a linear terminal chain of eight carbon atoms and caprohydroxamic acid, having a linear chain of ten carbon atoms. Such alkylhydroxamic acids may be used alone or in combination and in amounts as noted above for an optional solubilizing agent.

[0107] Formulations prepared for personal care use, and pharmaceutical compositions, depending on the end use (topical or oral) may include any other colorants, fragrances, active ingredients or other additives typically used and/or to be developed in the art for use in personal care and pharmaceutical formulations, in which additives will vary depending upon the formulation in which the preferred bio-1,2-alkanediols, or antimicrobial products or systems containing the bio-1,2-alkanediols are used, for example, in topical skin toners, skin cleansers, night creams, skin creams, shaving creams, skin care lotions, or other cosmetic preparations; make-up, such as foundation, liquid and powder-based make-up, mascara, lipstick, blush, gloss, eye-liner and the like; or other personal care and/or pharmaceutical compositions, such as, sunscreens, lip balms, fragrances, massage oil, shampoos, conditioners, conditioning shampoos,

hair styling gels, hair reparatives, hair tonics, hair fixatives, hair mousses, bath and shower gels, liquid soaps, moisturizing sprays, makeup, pressed powder formulations, bath additives, ophthalmic preparations, foaming soaps and body washes, sanitizing wipes, hand sanitizers, medicaments (tablets or liquid), towelettes and wipes and others. It should be understood, based on this disclosure that a wide variety of personal care and pharmaceutical compositions could benefit from the properties of the bio-1,2-alkanediols of the present invention, wherein, as used herein, pharmaceutical composition is one having at least one active pharmaceutical ingredient (API).

[0108] The personal care and pharmaceutical formulations, if liquid based (such as gels, hydrogels, lotions, shampoos, liquid pharmaceuticals and the like) will also preferably include water as part of the liquid base. The formulations and compositions may include other additives as well depending on the end formulation desired, such as without limitation, at least one humectant, at least one emulsifier and/or thickener, chelating agent(s), gelling agent(s), amino acid(s), emollient(s), various solvents, free radicals and initiators, sunscreen UVA and/or UVB blocking agents, antioxidants, other preservatives, waxes, polymers and copolymers, inorganic and organic pigments and/or one more fragrances, favoring(s), coloring agent(s), herbs, natural extracts, essential oils, pharmaceutical drug products, other APIs and other additives commonly used in such formulations.

[0109] Personal care and pharmaceutical compositions using the bio-1,2-alkanediols herein may be lotion-based, oil-in-water emulsions, water-in-oil emulsions, water-in-silicone emulsions, silicon-in-water emulsions, gels, solids, liquids, cream based, oil based, aqueous/alcoholic or glycolic solution based, dispersions, suspensions or syrups, microemulsions or a liposome-based formulations.

[0110] In water-based formulations, other than solids and thicker gels, etc., it is preferred that about 20% by weight to about 95% by weight (on a wet basis) of water is incorporated therein. The various additives aside from the water and preferred antimicrobial systems noted herein, would make up the remaining portion of various personal care and pharmaceutical compositions. Preferably, each additive is present in an amount of up to about 75 percent by weight of the entire formulation, and more preferably up to about 40 percent by weight, with a collective amount of such additives of preferably no greater than about 50 percent by weight.

[0111] In a household product, antimicrobials are also useful additives. Household product compositions can include household cleaners as well as fabric care compositions. Cleaning

compositions (whether solids or solutions) can incorporate cleaning agents that are active ingredients for cleaning (bleach, vinegar, ammonia, citric acid and the like). For liquid cleaning agents, aqueous solutions may be used as are known in the art or to be developed, such as quaternary ammonium compounds, bleach, vinegar, or basic or acidic cleansers. Commercially available quaternary ammonium-based cleaning products include various antibacterial all-purpose cleaners among others which are intended and well-suited for sanitizing or disinfecting efficacy, however, such compositions still incorporate antimicrobials and other preservatives for shelf life and to prevent growth of foreign agents. Thus, such compositions also benefit from use of the natural bio-1,2-alkanediols herein.

[0112] For more natural cleaning solutions, such as citric acid-based agents or other green cleaning agents (ecologically friendly), consumers would be interested in further additives that are also natural, and in this case that are derived from a biological source. Thus, such compositions benefit from natural bio-based 1,2-alkanediols herein as well as antimicrobial systems and products incorporating the bio-1,2-alkanediols. Such natural cleaning compositions as well as standard cleaning compositions as noted above may also incorporate various optional additives in varying amounts as noted below. Citric acid-based cleaning products may include lemon, orange or grapefruit-based cleaning agents. Other suitable components may include grape seed oil, vegetable oils combined with one or more of mild peroxide agents, surfactants, and the like, as well as pigment(s) or colorant additive(s) to provide a visual alerts when the cleaners are present, conventional or alternative preservation compound(s), antimicrobial(s), bactericide(s) or fungicide(s) (each of which may be used along or in combination with the bio-1,2-alkanediols of the present invention in an antimicrobial system or product), thixotropic agents and rheological modifiers, pH adjusting additives or buffers, as well as fragrance additive(s) for providing a clean smell (pine scent, lemon scent, orange scent, floral scent, etc.). In addition, other agents for foaming, color change or effervescence (bubbling) may be provided if desired to demonstrate cleaning action. Solid cleaners can incorporate similar additives, but can be compressed, incorporated or formed from depositing a cleaning material on a substrate (sponge, scrubber, mop head or the like), and various inactive agents for holding the solid cleaning material together (hardeners, gelling agents, mineral powder and the like). Other additives for household cleaning compositions may include pH buffering agent(s), a fragrance encapsulate(s) or carrier(s), fluorescer(s), hydrotrope(s), soil-release agent(s), polyelectrolyte(s), enzyme(s), optical brightening agent(s),

anti-oxidant(s), UV absorbing compound(s), propylene glycol, dipropylene glycol, opacifier(s), pearlescent(s) and combinations of these as well as other cleaning product additives known or to be developed.

[0113] The fabric care compositions can include any active fabric cleaning component as well as various conditioning components as are known or to be developed in the art. Such compositions may include ingredients used for fabric cleaning or laundering, fabric conditioning or softening, fabric dye(s), water conditioner(s) and/or fabric care composition(s) such as spot removers or stain treatments. Such ingredients include without limitation antifoam agent(s), antideposition agent(s), fragrance(s) and their carrier(s) or encapsulate(s), traditional or conventional diols (although such diols may be omitted if the bio-1,2-alkanediols are useful in the same or an enhanced or boosted capacity for an existing diol), colorant(s) such as pigment(s) or dye(s), and co-softening agent(s). Others additives for fabric care compositions may include, without limitation, other traditional preservative(s), antimicrobial(s), bacteriocide(s), and/or fungicide(s)(each of which may be used alone or in an antimicrobial product or system as described herein), pH modifier(s) or buffering agent(s), fluorescer(s), hydrotrope(s), soil-release agent(s), polyelectrolyte(s), enzyme(s), optical brightening agent(s), anti-shrinking agent(s), anti-wrinkle agent(s), anti-spotting agent(s), anti-oxidant(s), UV absorbing compound(s), anti-corrosion agent(s), drape imparting agent(s), anti-static agent(s), ironing aid(s), odor-preventing compound(s), perfume encapsulate(s), cotton seed oil, tea tree oil, aloe vera extract, propylene glycol, dipropylene glycol, opacifier(s), pearlescent(s) and combinations of these components.

[0114] The antimicrobial bio-1,2-alkanediols herein may also be used in the treatment of the finished textile(s) and/or treatment of the fibers or yarns from which a textile is to be fabricated to achieve the desired benefit. Textiles may include woven and non-woven textiles, such as felt and tapa cloth and other bark cloths, or blends and combinations of the same. Textile fiber (whether it exists in finished textile form, yarn or fiber form) may be any known or developed in the art and include synthetic fibers, "natural" fibers, such as animal derived fibers or cellulosic/plant-derived fibers and blends or combinations of any of these.

[0115] Animal-derived fibers may include and derived from the hairs or fur of an animal. Examples are, without limitation, lambs or sheep's wool, alpaca, angora wool, azlon, byssus, camel hair, cashmere wool, chiengora, chatgora, llama, mohair wool, qiviut, rabbit, silk, vicuna, yak, pashmina wool and combinations of the same. Cellulosic or plant-derived fibers may

include, without limitation, those obtained from flax (linen fibers), cotton, ramie, jute, kenaf, beach hibiscus, roselle, urena, hemp (e.g., Crotalaria juncea, Cannabis sativa, Apocynum cannabinum), hoop vine, sisal, henequen, yucca, abaca, genus Sansevieria, New Zealand flax, cotton, coir, milkweed, kapok, floss silk, Proboscidea parviflora, bamboo, bast, fique, banana, modal, lyocell, pina, raffia, rayon, soy protein, acetate and combinations of the same. Synthetic fibers may include any known or to be developed, such as for example, and without limitation, acrylic, Kevlar®, modacrylic, Nomex®, nylon, polyester, lycra, spandex, rayon, and combinations of the same.

[0116] Fabric treatment compositions may be applied to the textile or fibers. The compositions may be applied as either a wet or dry composition and during a laundering cycle with water or a drying cycle. Such fabric treatment materials may be used for softening and/or conditioning a textile or fiber; reducing and/or preventing wrinkles, imparting fragrances to a textile or fiber; reducing ironing time, improving softness and the like.

[0117] The invention also incorporates use of the 1,2-bio-alkanediol materials formed according to the invention as a material for boosting the antimicrobial efficiency of existing antimicrobials, preservatives, alternative preservation materials and/or hurdle technologies.

[0118] By boosting the antimicrobial efficacy, it is meant that the antimicrobial efficacy of an existing antimicrobial and/or preservative (including alternative preservation materials or hurdle technologies) when combined with the 1,2-bio-alkandiols achieve an improvement of antimicrobial effectiveness that is more than insubstantial, *i.e.*, at least about 5%, preferably at least about 10%, and more preferably at least about 20% or more improvement, while providing a natural boosting material. Boosting effects and antimicrobial effects in a formulation are evaluated by measuring performance using a preservative efficacy test ("PET") or a challenge test. Preservatives and antimicrobials used in cosmetic, toiletry and pharmaceutical products must enable the products to successfully pass microbiological testing protocols, known as "challenge tests," established by government regulations and trade organizations. Challenge tests are performed by adding known quantities of microorganisms to a product and measuring the increase or decrease in microorganism population over time. The organisms include Gram-positive bacteria, Gram-negative bacteria, yeast and mold. The Cosmetic, Toiletries, and Fragrance Association (CTFA) has defined a challenge test that is widely accepted as the standard in the cosmetic, toiletry and pharmaceutical industry. The test requires that the quantity of bacteria be reduced by 99% in seven days, and that the quantity of yeast and fungi

(mold) be reduced by 90% in seven days. In order to pass a challenge test, the product must contain the appropriate amounts and types of preservative compounds that will enable antimicrobial efficacy against a broad spectrum of microorganisms in a short period of time.

[0119] In addition to the content noted to provide antimicrobial efficacy, if using as a boosting material to improve the effectiveness of an existing antimicrobial and the like as noted above it is preferred that the 1,2-bioalkanediol(s) are incorporated in an amount of about 0.1 to about 10 weight percent, and preferably 5.0 to about 3.0 weight percent, of the total composition; and in a ratio of about 99.999:0.001 to about 0.001:99.999, and preferably about 99.9:0.1 to about 0.1:99.9 of the total amount of existing antimicrobial, preservative, alternative preservation and/or hurdle technology components already existing in the composition.

[0120] The invention will now be described with respect to the following non-limiting examples:

EXAMPLES

[0121] Bio-1-octanol is formed from the hydrogenation of bio-octanoic acid (suitable sources of which may be derived from coconut, palm or any other renewable source or process that can produce octanoic acid). The bio-1-octanol is dehydrated regioselectively by feeding the bio-1-octanol at an elevated temperature into a fixed bed reactor containing a catalyst according to the invention herein.

[0122] Gas Chromatography (GC) was an important method used to characterize both petroleum and natural-renewable derivatives. Products (*e.g.* octenes) were characterized using a Thermo Scientific Trace 1310 Gas Chromatograph employing an FID detector and Chromeleon software (version 7.2.4.8525). For dehydration reactions products the GC employed a Restek MXT-5 column (30 m length, 0.5 μm film, 0.53 ID), helium carry gas (3.0 mL/min), CT split injection 45 mL/min (5.0 mL/min purge flow), injector 250 °C, detector 300 °C, oven 70 °C hold for 8 min, then ramp to 300 °C (15 °C/min) with a final hold for 6.67 min. For alkanediol products GC analysis employed a Restek MXT-WAX column (30 m length, 0.5 μm film, 0.53 ID), helium carry gas (5.0 mL/min), CT split injection 10 mL/min (5.0 mL/min purge flow), injector 220 °C, detector 250 °C, oven 70 °C hold for 0.25 min, then ramp to 250 °C (10 °C/min) with a final hold for 6.67 min.

EXAMPLE 1

[0123] γ-Alumina powder was treated with an aqueous solution of calcium acetate using the technique of incipient wetting to afford a catalyst containing 1.50% calcium (based on CaO) after calcination in air at 440°C for a period of 12 h.

EXAMPLE 2

[0124] γ-alumina powder was treated with an aqueous solution of calcium acetate using the technique of incipient wetting to afford a catalyst containing 1.50% calcium (based on CaO) after calcination in air at 500°C for a period of 12 h.

EXAMPLE 3

[0125] Catalysts prepared in EXAMPLE 1 and EXAMPLE 2 were loaded into separate 75 mL (Sigma Aldrich Part No. Z173592) reactors, each was wrapped with heating tape and covered with fiberglass insulation. The temperature was controlled by affixing a thermocouple to the outside skin of the reactor, this input was used for a temperature controller. Bio-1-octanol was fed into the reactor maintained at 315°C using an HPLC pump. The bio-1-octanol feed rate was adjusted in a manner to obtain conversion more than 95%, but less than 100%. After 1 h of continuous operation a sample was collected and analyzed for analyzing chemical conversion of the bio-1-octanol and regioselectivity of bio-1-octene. The results are shown below:

Table 2

Catalyst	Calcination Temperature (°C)	1-Octene (%)	2-Octene & 3-Octenes (%)	1-Octanol (%)	1-Octene Selectivity (%)
EXAMPLE 1	440	94.0	3.2	1.6	97.4
EXAMPLE 2	500	88.9	6.6	3.5	93.1

EXAMPLE 4

[0126] γ-alumina in the form of 1/16" extrudate, Porocel® CatGuard® was cut to have length to diameter ratios in the range of 2 to 4. The extrudate was modified with an aqueous solution of calcium acetate. The weight of solution to alumina was 0.55 by weight and the calcium acetate concentration was at level to deliver 1.50% of CaO (after calcination). This catalyst was subjected to calcination in air at 440°C for a period of 12 h.

EXAMPLE 5

[0127] The 48 g of the catalyst prepared in EXAMPLE 4 was loaded into a 75 mL (Sigma Aldrich Part No. Z173592) reactor, wrapped with heating tape, and covered with fiberglass insulation. The temperature was controlled by affixing a thermocouple to the outside skin of the reactor, this input was used for a temperature controller. Bio-1-octanol was fed at 0.2 mL/min into the reactor maintained at 315°C. After >1,400 h of TOS, that included regular shut-downs and start-ups, catalyst performance with regard 1) chemical conversion of the bio-1-octanol, 2) product selectivity, 3) and regioselectivity for bio-1-octene was unchanged. A GC chromatogram of the crude product collected from the reactor is shown in Fig. 3 with an octene selectivity of 96% and with chemical yield of bio-1-octene of 94%.

EXAMPLE 6

[0128] The product in EXAMPLE 5 was subjected to simple distillation at atmospheric pressure. The product obtained was analyzed by GC and the chromatogram is shown in Fig. 4. The product from the distillation was 99.9% bio-octenes with a 96.7% content of bio-1-octene.

EXAMPLE 7

[0129] The product in EXAMPLE 6 was converted to the bio-1,2-octanediol by treatment with formic acid and peroxides, then a base hydrolysis, and finally purified by fractional distillation. The GC chromatogram is shown in Fig. 5. The bio-1,2-octanediol obtained in this example has a chemical purity 98.7% by GC analysis. A typical GC chromatogram of the petro-1,2-octanediol currently used in commercial cosmetic applications is displayed in Fig. 6.

EXAMPLE 8

[0130] Stable isotope analyses were carried out on petroleum-based and those prepared from the natural and renewable feedstocks prepared in EXAMPLES 6 and 7. The values are shown below:

Table 3

Compound	$\delta^{13}C$	$\delta^{2}H$
Bio-1-Octanol	32.3	-273
1-Octanol (petro-based)	30.3	-87
Bio-1-Octene	32.0	-288
1-Octene (petro-based)	31.8	Not tested
Bio-1,2-Octanediol	32.2	-245
1,2-Octanediol (petro-based)	31.5	-50

EXAMPLE 9

[0131] The bio-1,2-octanediol prepared in EXAMPLE 7 was subjected to testing that is currently used to qualify the petroleum, non-renewable, non-natural equivalent. The bio-1,2-octanediol prepared in EXAMPLE 7 was found to meet all the batch analytical testing requirements:

Table 4

Analysis	Natural 1,2-octanediol	Petroleum 1,2-octanediol	Specification
Odor	Conforming	conforming	mild
Color, Lovibond (yellow)	0.1	0.1	≤ 1.5
Color, Lovibond (red)	0.0	0.0	≤ 0.3
Sediment	Conforming	Conforming	No discoloration
Color, APHA 142	8	1	≤ 100
COLOR, APHA 142-01	8	1	≤ 30
Infrared Spectrum	Conforming	Conforming	Matches Std.
Hydroxyl value Mg KOH/g	761	740	740 to 770
Moisture % w/w	0	0	≤ 2
Appearance	Conforming	Conforming	Clear liquid above 35 °C
Assay, %	98.7	99.5	≥ 98.0
% 1,2-octane oxide	0.1	0.1	Report result
Color 999-03	Conforming	Conforming	Matches Standard

EXAMPLE 10

[0132] In a comparative example, bio-1-octanol was fed into a 75 mL reactor packed with a catalyst prepared as follows: gamma-alumina powder was modified with a sodium hydroxide solution (5 wt-% NaOH) to create a second catalyst, the second catalyst was dried in an oven and then treated with diethoxydiphenylsilane (1 wt-% based on alumina) dissolved in ethanol. The solvent was removed, the catalyst washed with ethanol, and dried in an oven to create a

third catalyst. This third catalyst was calcined at 400°C for 12 h. The catalyst was loaded into a 75 mL reactor, heated to a target temperature of 325°C and bio-1-octanol feed rates were adjusted to optimize both conversion and regioselectivity.

EXAMPLE 11

[0133] Petro-1-hexanol was fed into a 75 mL reactor packed with the catalyst prepared in EXAMPLE 4. The catalyst used in this example had greater than 1,400 h of TOS used for bio-1-octanol dehydration to bio-1-octene. For this series of dehydration reaction examples, the temperature was varied from 330°C to 370°C and the feed rate was adjusted in order to achieve between 1 and 2% of hexanol passing through the reactor. The results for the hexanol dehydration are shown below:

Table 5

Catalyst	Reactor Temperature (°C)	1-Hexene (%)	2-Hexenes & 3-Hexene (%)	1-Hexanol (%)	1-Hexene Selectivity (%)
EXAMPLE 11A	330	92.8	3.5	1.8	95.8
EXAMPLE 11B	350	93.8	3.1	1.7	96.8
EXAMPLE 11C	370	90.1	3.2	1.6	96.6

[0134] In EXAMPLE 11C where the reactor is maintained at 370°C a new peak in the GC chromatogram appears have an area-% of 3.6; thus, indicating a lower chemical yield of 1-hexene and formation of another product.

EXAMPLE 12

[0135] After 1400 h of TOS for the dehydration of bio-1-octanol, some catalyst was removed at the entrance side of the tube reactor. In Fig. 7 the used catalyst is photographed next to catalyst with 0 h TOS. The used catalyst shows only a slight discoloration, and as noted herein, displays no loss in chemical conversion or loss in regioselectivity.

[0136] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is

understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

We claim:

1. A process for the synthesis of bio-1,2-alkanediols, comprising:

providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and

converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

2. The process of claim 1, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain of about 6 to about 14 carbon atoms.

3. The process according to claim 2, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain length of about 6 to about 10 carbon atoms.

4. The process according to claim 3, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain length of about 6 to about 8 carbon atoms.

5. The process according to claim 1, wherein the bio-alkene is bio-octene and the bio-1,2-alkane diol is bio-1,2-octanediol.

6. The process according to claim 1, wherein the bio-alkene results from a process wherein a bio-1-alcohol is dehydrated by heating the bio-1-alcohol in a reactor with a catalyst.

7. The process according to claim 6, wherein the reactor is a fixed bed reactor.

8. The process according to claim 7, wherein the fixed bed reactor is a fluidized fixed bed reactor.

9. The process according to claim 6, wherein the catalyst is selected from $ZnAl_2O_4$ and a ɤ-alumina catalyst.

10. The process according to claim 9, wherein the bio-alkene has a bio-1-alkene regioselectivity of about 92% to about 99%.

11. The process according to claim 10, wherein the bio-alkene have a bio-1-alkene regioselectivity of about 95% to about 99%.

12. The process according to claim 1, wherein the process yields at least about 92% to about 99% of the bio-1,2-alkanediol.

13. The process according to claim 9, wherein the catalyst is a γ-alumina catalyst is treated with a base to form a modified γ-alumina catalyst.

14. The process according to claim 13, wherein the base comprises a Group I or a Group II metal.

15. The process according to claim 9, wherein the γ-alumina catalyst is treated with a calcium promoter to provide a modified γ-alumina catalyst.

16. The process according to claim 15, wherein the modified γ-alumina catalyst is calcined to provide a calcined γ-alumina catalyst.

17. The process according to claim 16, wherein the calcium promoter is used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination.

18. The process according to claim 17, wherein the calcium promoter is used in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination.

19. The process according to claim 15 wherein a temperature during calcination is about 400°C to about 500°C.

20. The process according to claim 19, wherein the temperature during calcination is about 420°C to about 480°C.

21. The process according to claim 20, wherein the temperature during calcination is about 440°C to about 460°C.

22. The process according to claim 15, wherein calcination is carried out in an oven.

23. The process according to claim 15, wherein the calcination is carried out in an atmosphere of air or inert gas.

24. The process according to claim 6, wherein the bio-alkene undergoes a distillation step to refine the bio-alkene prior to converting the bio-alkene to the bio-1,2-alkanediol.

25. The process according to claim 6, wherein the bio-1,2-alkanediol formed from the bio-alkene undergoes a final distillation step to refine the bio-1,2-alkanediol.

26. The process according to claim 1, wherein the bio-alkene results from a process wherein the bio-1-alcohol in water is dehydrated by heating the bio-1-alcohol with a catalyst under a purge gas.

27. The process according to claim 1, wherein the bio-alkene is converted to the bio-1,2-alkanediol by reacting the bio-alkene in the presence of at least one of formic acid or acetic acid and a peroxide to form a bio-1,2-epoxyalkane having an epoxy ring, and contacting the 1,2-epoxyalkane with water and sodium hydroxide to form the bio-1,2-alkanediol.

28. The process according to claim 1, wherein the process yields at least about 60% to about 99% of the bio-1,2-alkanediol.

29. The process according to claim 28, wherein the process yields at least about 72% to about 99% of the bio-1,2-alkanediol.

30. A process for making bio-1,2-alkanediols, comprising:

providing a bio-1-alcohol and a catalyst treated with a base;

dehydrating the bio-1-alcohol in the presence of the catalyst to form a bioalkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and

converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

31. The process according to claim 30, wherein the catalyst is a γ-alumina catalyst and the base comprises calcium.

32. The process according to claim 31, wherein the γ-alumina catalyst is treated with a calcium promotor and after treatment is calcined at a temperature of about 400°C to about 500°C.

33. The process according to claim 30, wherein the process yields about 72% to about 99% of the bio-1,2-alkanediol.

34. The process according to claim 30, wherein the bio-1-alkene regioselectivity is about 95% to about 99%.

35. A method for treating a catalyst for use in dehydration of alcohols, comprising

providing a γ-alumina catalyst;

treating the γ-alumina catalyst with a base comprising a Group I or a Group II metal; and

heating the γ-alumina catalyst to a temperature of about 400°C to about 500°C.

36. The method according to claim 35, wherein the base comprises calcium.

37. The method according to claim 36, wherein the base is a calcium promoter and the heating occurs during calcination.

38. The method according to claim 37, wherein the calcium promoter includes is used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination.

39. The process according to claim 38, wherein the calcium promoter is used in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination.

40. The process according to claim 35, temperature during calcination is about 420°C to about 480°C.

41. The process according to claim 40, wherein the temperature during calcination is about 440°C to about 460°C.

42. A composition, comprising at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

43. The composition according to claim 42, wherein the composition is a personal care composition.

44. The composition according to claim 43, wherein the personal care composition is a hair care composition, an oral care composition, a skin care composition or a cosmetic composition.

45. The composition according to claim 42, wherein the composition is a composition for a household product.

46. The composition according to claim 45, wherein the household product is a fabric care product or a cleaning product.

47. The composition according to claim 42, wherein the composition is an industrial composition.

48. The composition according to claim 42, wherein the composition is a pharmaceutical composition, a vitamin composition, or a health care composition.

49. The composition according to claim 42, comprising a second bio-1,2-alkanediol, different than the first bio-1,2-alkanediol, the second bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a second bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

50. The composition according to claim 49, wherein the composition further comprises at least one other bio-compound different from the first and the second bio-1,2-alkanediols.

51. The composition according to claim 50, wherein the composition comprises an antimicrobial compound different from the first and the second bio-1,2-alkanediol and different from the other bio-compound.

52. The composition according to claim 42, wherein the composition further comprises at least one other bio-compound different from the at least one bio-1,2-alkanediol.

53. The composition according to claim 52, wherein the composition comprises at least one antimicrobial compound different from the at least one bio-1,2-alkanediol and different from the other bio-compound.

54. The composition according to claim 42, wherein the first bio-1-alkene has a regioselectivity of about 95% to about 99%.

55. The composition according to claim 42, wherein the first bio-alkene is bio-octene and the at least one first bio-1,2-alkane diol is bio-1,2-octanediol.

56. A method for providing an antimicrobial effect to a composition, including incorporating an antimicrobial system to the composition, wherein the antimicrobial system comprises at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of at least one first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

57. The method according to claim 56, wherein the antimicrobial system further comprises a second bio-1,2-alkanediol different than the first bio-1,2-alkanediol, wherein the first bio-1,2-alkanediol has a carbon chain length of about 5 to about 20 carbon atoms and is formed by conversion of a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

58. The method according to claim 57, wherein the composition further comprises at least one other bio-compound different from the first and the second bio-1,2-alkanediols.

59. The method according to claim 58, wherein the antimicrobial system comprises at least one other preservative compound different from the first and the second bio-1,2-alkanediol and different from the other bio-compound.

60. The method according to claim 57, wherein the composition further comprises at least one other bio-compound different from the at least one first bio-1,2-alkanediol.

61. The method according to claim 60, wherein the antimicrobial comprises at least one other antimicrobial compound and/or preservative compound different from the at least one first bio-1,2-alkanediol and different from the other bio-compound.

62. The method according to claim 57, wherein the antimicrobial system demonstrates antimicrobial efficacy.

63. The method according to claim 57, wherein the first bio-1-alkene has a regioselectivity of about 95% to about 99%.

64. The method according to claim 57, wherein the first bio-alkene is bio-octene and the at least one first 1,2-alkane diol is bio-1,2-octanediol.

65. A method for boosting the antimicrobial efficiency of an antimicrobial and/or a preservative in a composition, comprising incorporating an antimicrobial system into the composition, wherein the second antimicrobial system comprises at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

66. The method according to claim 65, wherein the antimicrobial system further comprises a second bio-1,2-alkanediol different than the first bio-1,2-alkanediol, wherein the second bio-1,2-alkanediol has a carbon chain length of about 5 to about 20 carbon atoms and is formed by conversion of a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

67. The method according to claim 66, wherein the composition further comprises at least one other bio-compound different from the antimicrobial and/or preservative and different from the first and the second bio-1,2-alkanediols.

68. The method according to claim 65, wherein the composition further comprises at least one other bio-compound different from the at least one first bio-1,2-alkanediol.

69. The method according to claim 65, wherein the first bio-1-alkene has a regioselectivity of about 95% to about 99%.

70. The method according to claim 65, wherein the antimicrobial system demonstrates antimicrobial efficacy.

71. The method according to claim 65, wherein the first bio-alkene is bio-octene and the at least one first bio-1,2-alkane diol is bio-1,2-octanediol.

72. An antimicrobial product, comprising at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

73. The antimicrobial product according to claim 72, further comprising a second bio-1,2-alkanediol, different than the at least one first bio-1,2-alkanediol, the second bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms and formed by conversion of a second bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

74. The antimicrobial product according to claim 73, wherein the product further comprises at least one other bio-compound different from the at least one first and the second bio-1,2-alkanediols.

75. The antimicrobial product according to claim 74, further comprising a second antimicrobial and/or a preservative different from the antimicrobial product.

76. The antimicrobial product according to claim 72, wherein the product further comprises at least one other bio-compound different from the at least one first bio-1,2-alkanediol.

77. The antimicrobial product according to claim 76, further comprising a second antimicrobial and/or a preservative different from the antimicrobial product.

78. The antimicrobial product according to claim 72, wherein the first bio-1-alkene has a regioselectivity of about 95% to about 99%.

79. The antimicrobial product according to claim 72, wherein the antimicrobial product demonstrates antimicrobial efficacy.

80. The antimicrobial product according to claim 72, wherein the first bio-alkene is bio-octene and the at least one first 1,2-alkane diol is bio-1,2-octanediol.

81. A product for boosting the efficacy of an antimicrobial and/or a preservative in a composition, the product comprising at least one first bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms which is synthesized by conversion of a first bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

82. The product according to claim 81, further comprising a second bio-1,2-alkanediol, different than the at least one first bio-1,2-alkanediol, the second bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms and formed by conversion of a second

bio-alkene, different than the first bio-alkene, having a carbon chain length of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

83. The product according to claim 82, wherein the composition further comprises at least one other bio-compound different from the at least one first and the second bio-1,2-alkanediols.

84. The product according to claim 81, wherein the product further comprises at least one other bio-compound different from the at least one first bio-1,2-alkanediol.

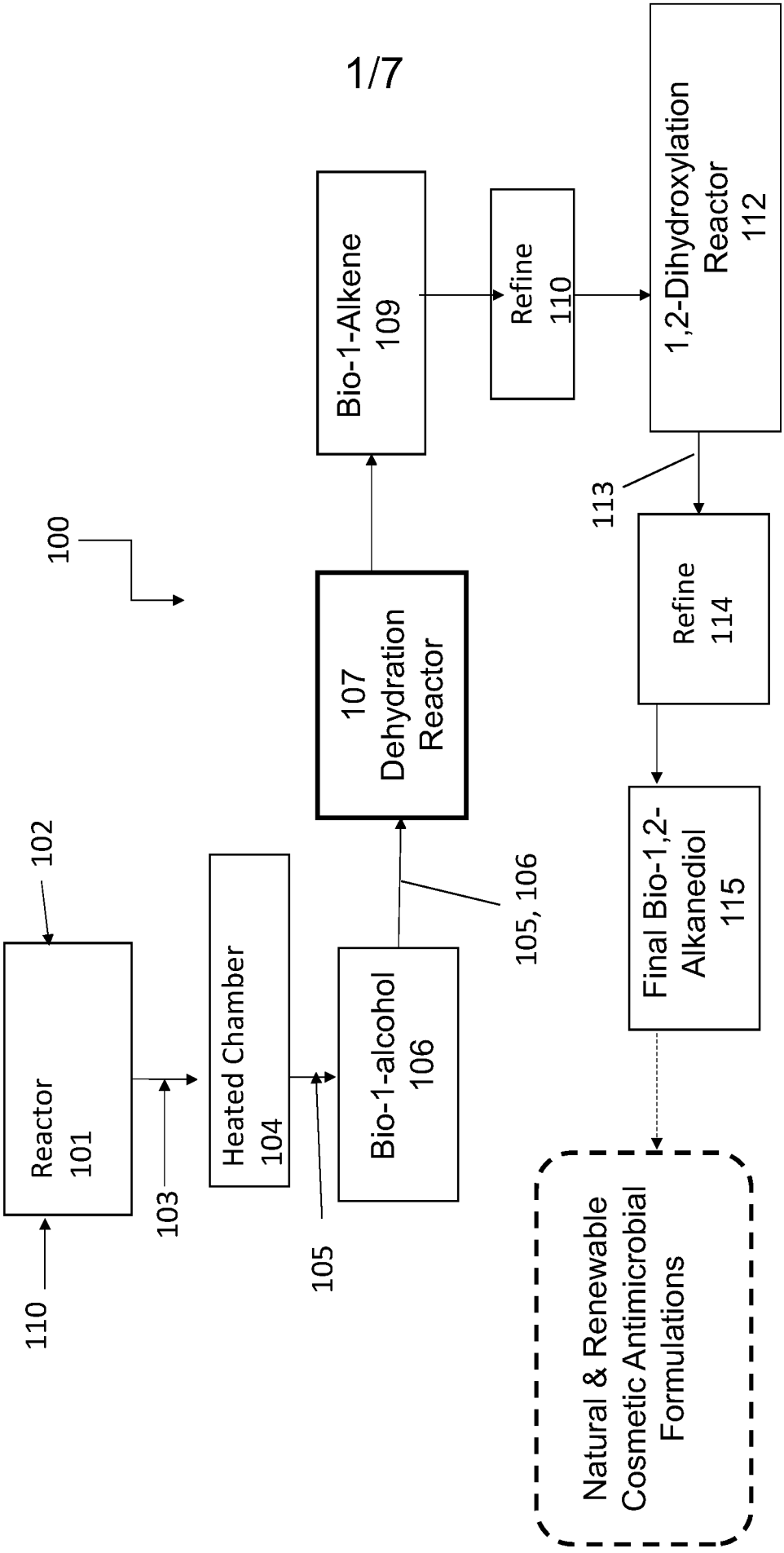
85. The product according to claim 81, wherein the first bio-1-alkene has a regioselectivity of about 92% to about 99%.

86. The product according to claim 82, wherein the first bio-alkene is bio-octene and the at least one first bio-1,2-alkane diol is bio-1,2-octanediol.

87. The product according to claim 81, wherein the product demonstrates antimicrobial efficacy.

ABSTRACT OF THE DISCLOSURE

A process is incorporated herein for the synthesis of bio-1,2-alkanediols, comprising: providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%, at least about 92% and/or at least about 95%; and converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms. Methods for treating catalysts which may be incorporated in the process for the synthesis of bio-1,2-alkanediols are also included herein. Such bio-1,2-alkanediols are used in compositions and products alone as antimicrobial materials, or with existing bio-compounds and/or antimicrobials, preservatives, alternative preservation systems and/or hurdle technology components. The bio-1,2-alkanediols incorporate a natural and bio-based pathway for antimicrobial effects in various compositions such as cosmetic, pharmaceutical, industrial and household products.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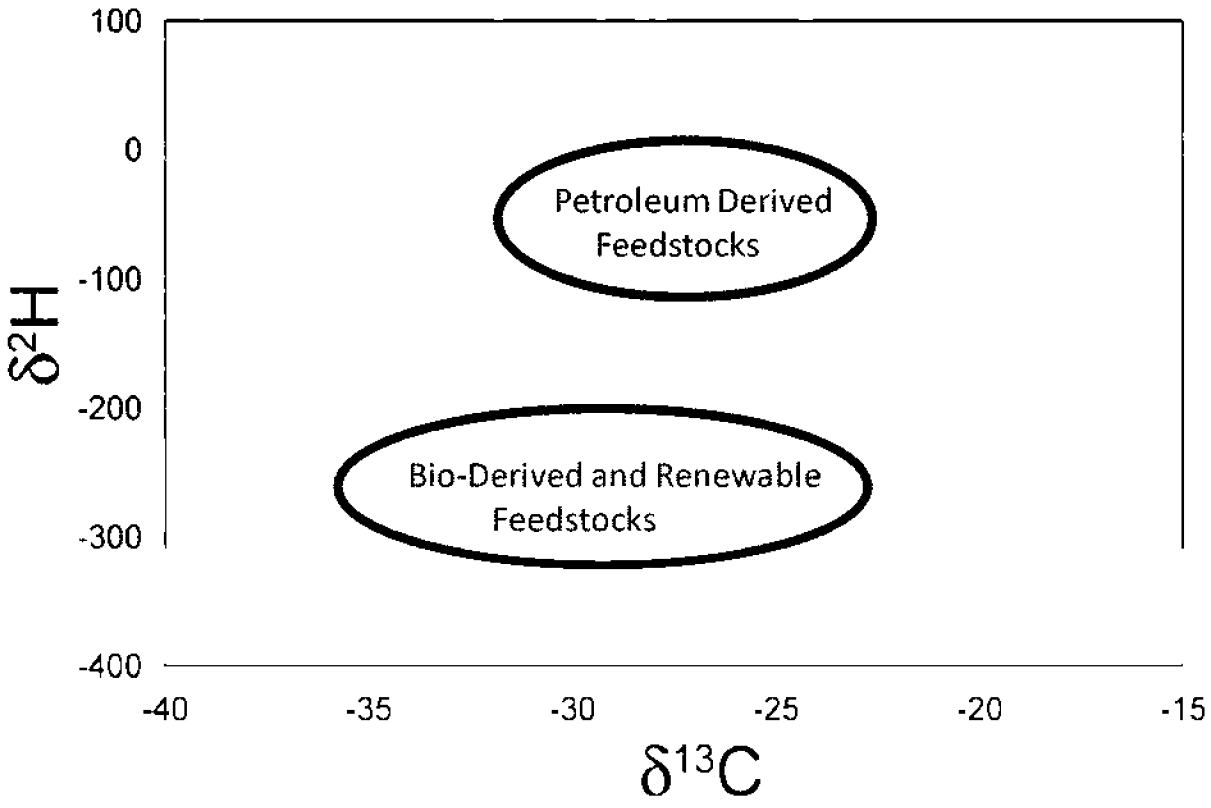
102
110
103
Heated Chamber 104
105
Bio-1-alcohol 106
105, 106
107 Dehydration Reactor
Bio-1-Alkene 109
Refine 110
1,2-Dihydroxylation Reactor 112
113
Refine 114
Final Bio-1,2-Alkanediol 115
Natural & Renewable Cosmetic Antimicrobial Formulations

Fig. 1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-200
-300
-400
δ^2H
Petroleum Derived Feedstocks
Bio-Derived and Renewable Feedstocks
-40
-35
-30
-25
-20
-15
$\delta^{13}C$

Fig. 2

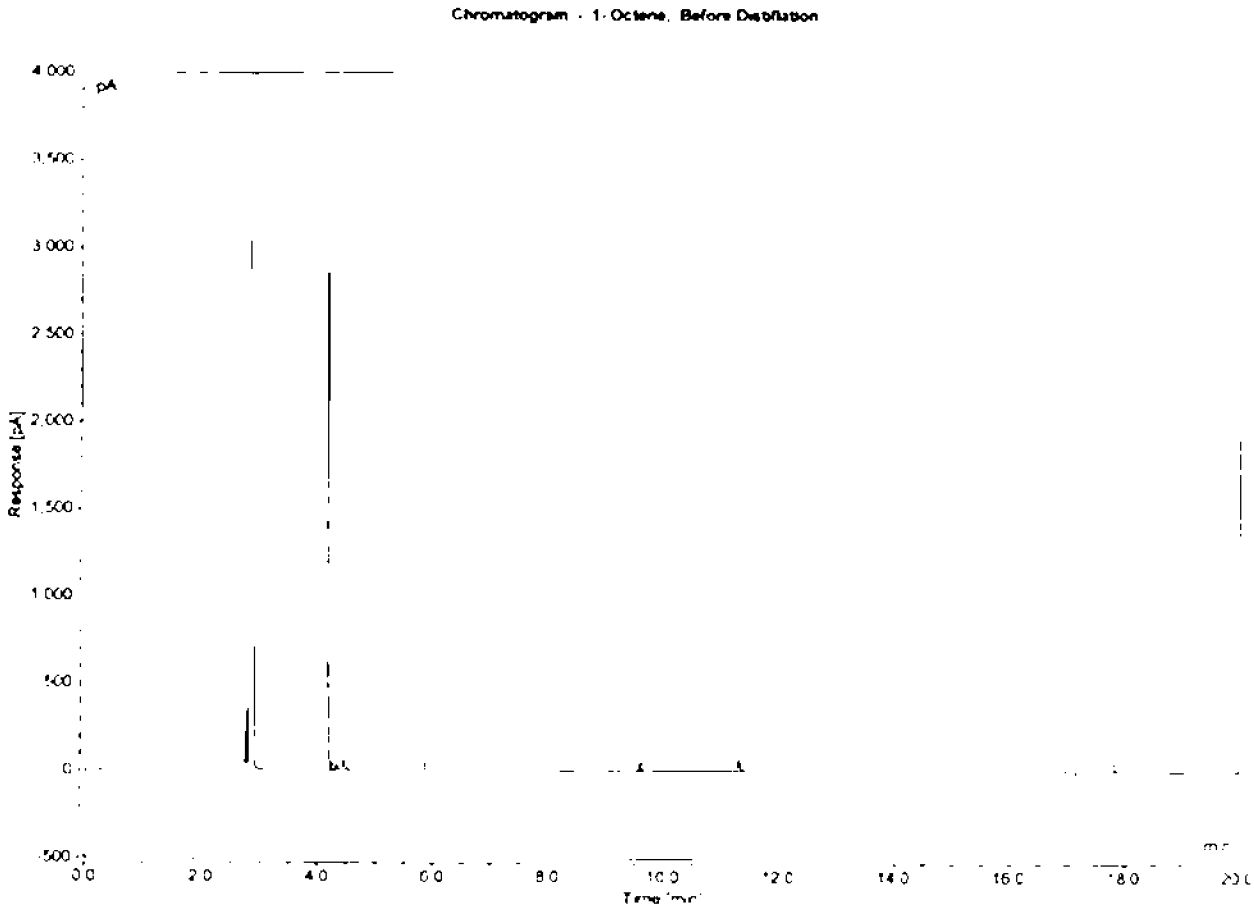
Chromatogram - 1-Octene, Before Destillation
pA
Response [pA]
4 000
3 500
3 000
2 500
2 000
1 500
1 000
500
0
-500
00
20
40
00
80
100
120
140
160
180
200

Fig. 3

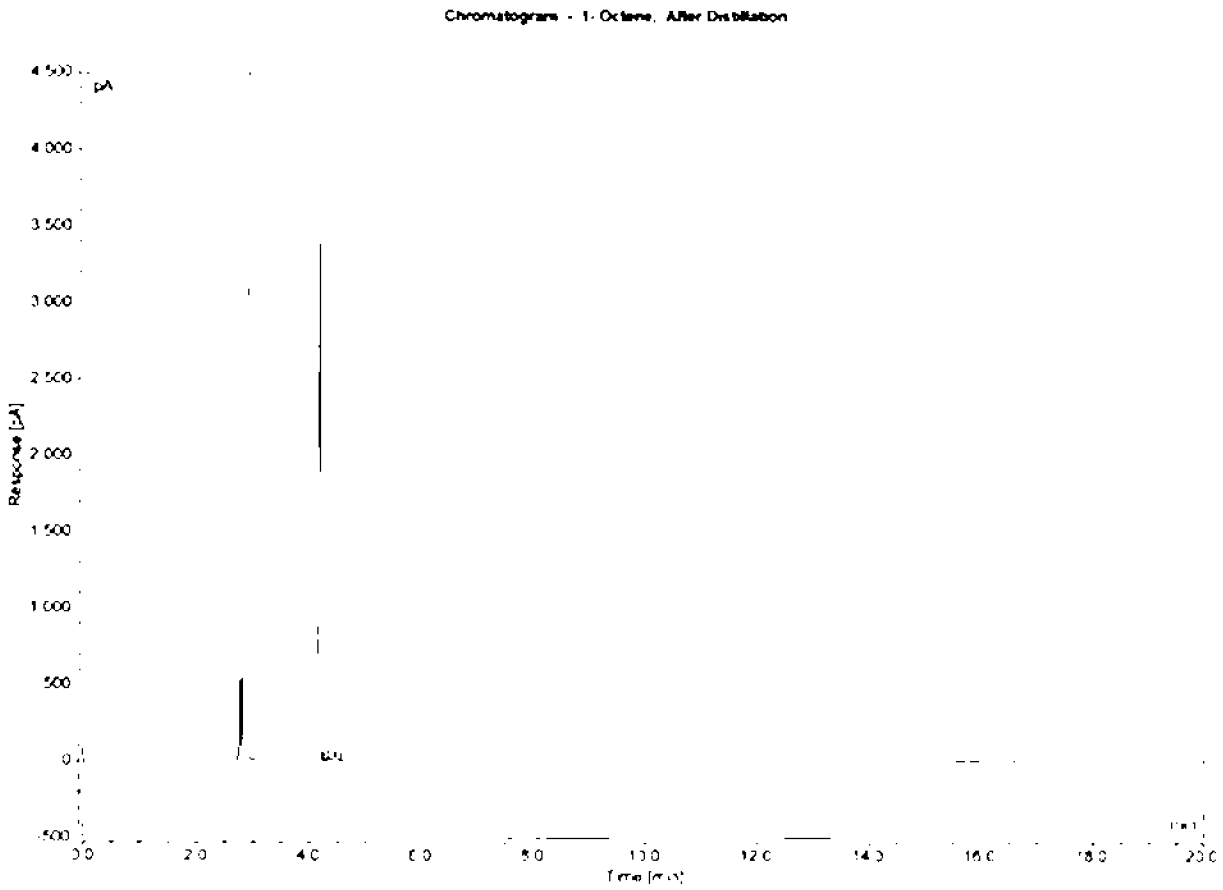
Chromatogram - 1-Octene, After Distillation
pA
4 500
4 000
3 500
3 000
2 500
2 000
1 500
1 000
500
0
-500
Response [pA]
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
Time [min]

Fig. 4

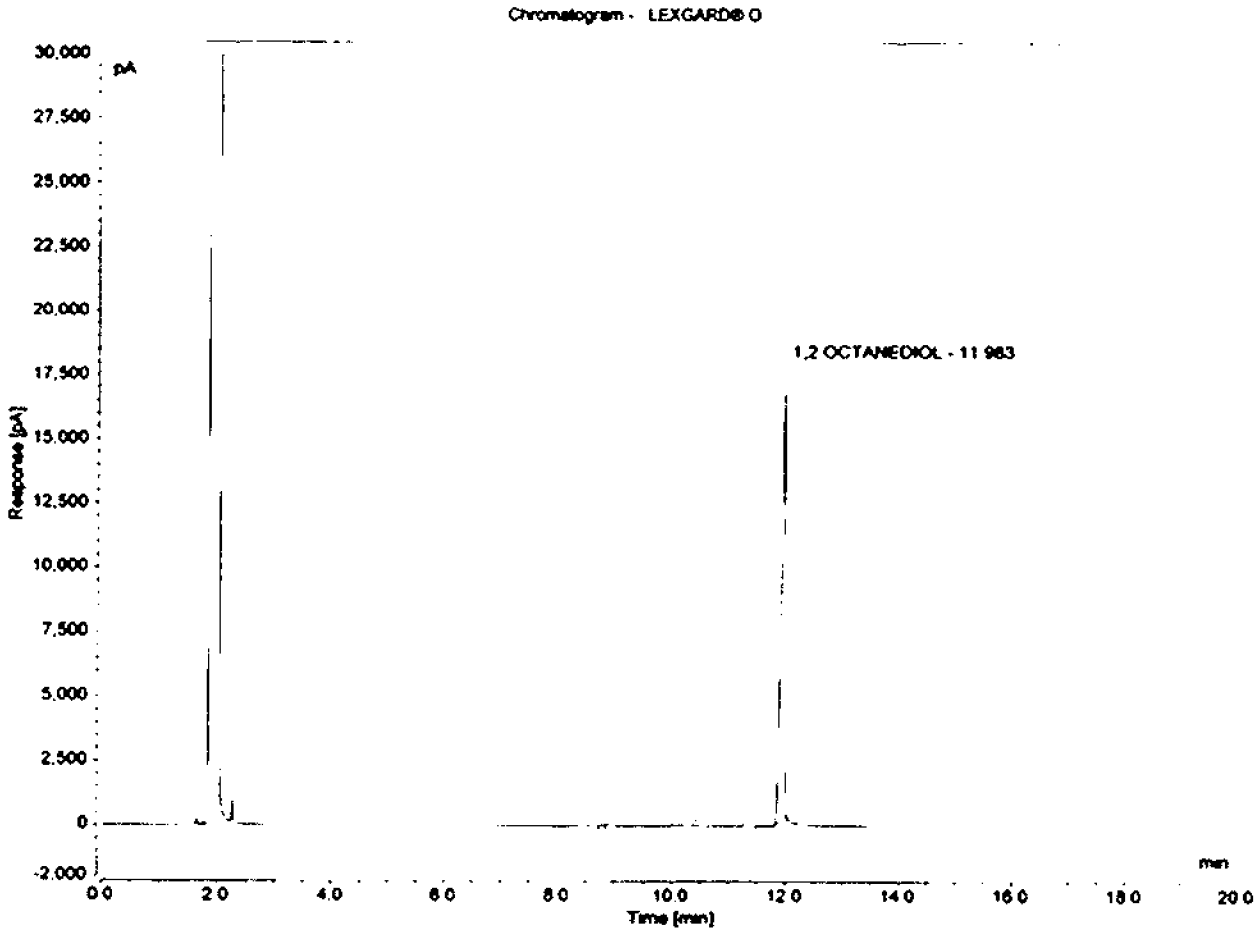
Chromatogram - LEXGARD® O
pA
30,000
27,500
25,000
22,500
20,000
17,500
15,000
12,500
10,000
7,500
5,000
2,500
0
-2,000
Response [pA]
1,2 OCTANEDIOL - 11.983
min
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
Time [min]

Fig. 5

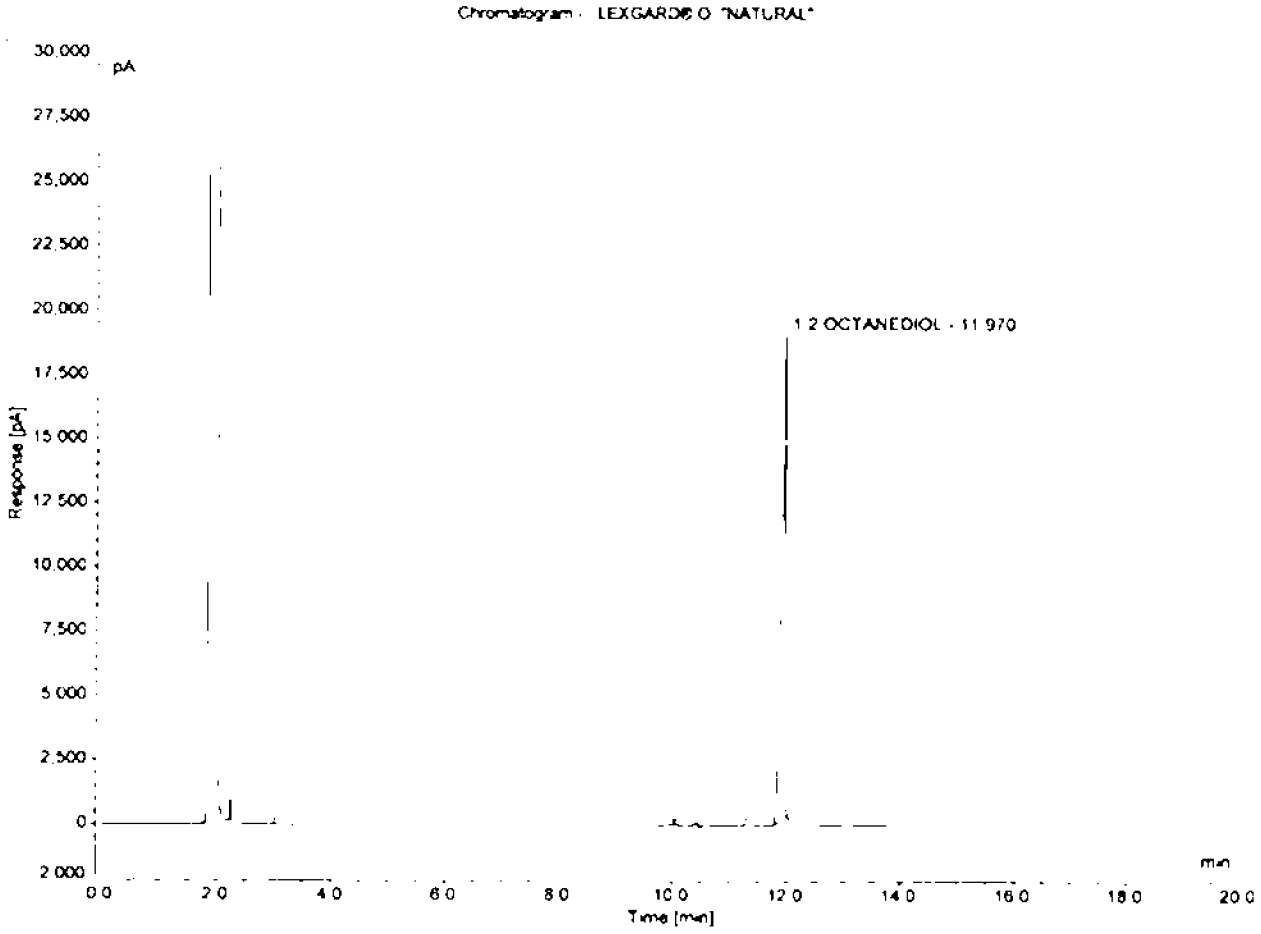
Chromatogram - LEXGARD® O "NATURAL"
30,000
pA
27,500
25,000
22,500
20,000
17,500
15,000
12,500
10,000
7,500
5,000
2,500
0
-2,000
Response [pA]
1,2-OCTANEDIOL - 11,970
min
0,0
2,0
4,0
6,0
8,0
10,0
12,0
14,0
16,0
18,0
20,0
Time [min]

Fig. 6

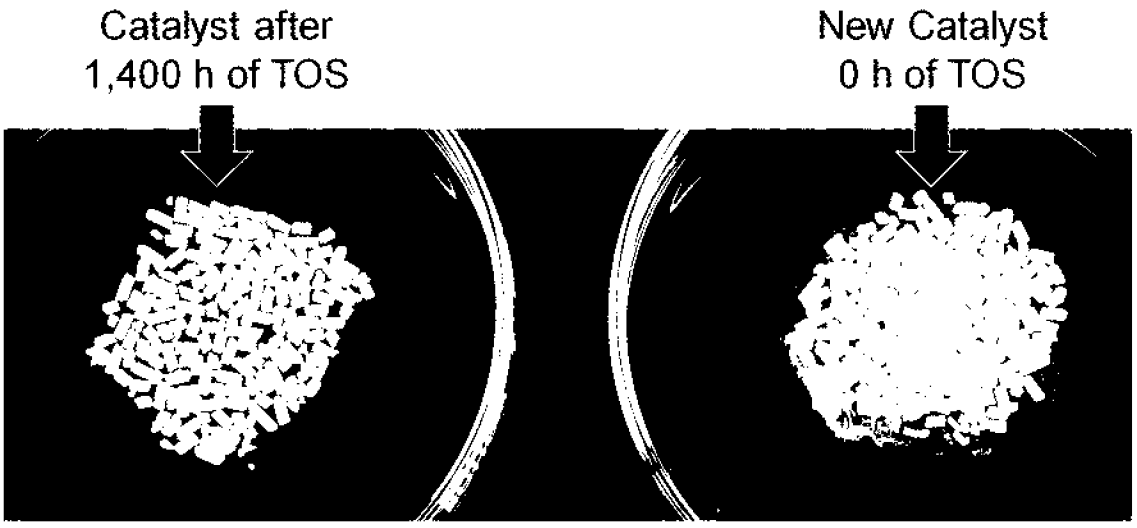

Fig. 7

DECLARATION
(Original application)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original sole inventor (if only one name is listed below) or an original joint inventor (if plural names are listed below) of the subject matter that is claimed and for which a patent is sought on the invention entitled:

NATURAL 1,2-ALKANEDIOLS, COMPOSITIONS HAVING NATURAL 1,2-ALKANEDIOLS AND PROCESSES FOR MAKING THE SAME.

the specification of which is attached hereto and/or was filed on _____ as Application No. _____.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to herein.

The above-identified application was made or was authorized to be made by me.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d), of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

FOREIGN PRIORITY APPLICATION(S)

			Priority Claimed
_____			[ ] Yes [ ] No
(Number)	(Country)	(Day/month/year filed)	
_____			[ ]Yes [ ] No
(Number)	(Country)	(Day/month/year filed)	

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional patent application(s) listed below:

PROVISIONAL PRIORITY PATENT APPLICATION(S)

		Priority Claimed
62/623,985	January 30, 2018	[X] Yes [ ] No
(Application No.)	(Filing Date)	
		[ ] Yes [ ] No
(Application No.)	(Filing Date)	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements made in this Declaration are punishable under 18 U.S.C. §1001 by fine or imprisonment of not more than five (5) years.

Full name of first or sole inventor Rocco V. Burgo

Inventor's Signature

Date

Residence Mullica Hill, New Jersey

Citizenship United States

Post Office Address 604 Widgeon Court, Mullica Hill, New Jersey 08062

Full name of second inventor Michael E. Wright

Inventor's Signature

Date

Residence Hurricane, Utah

Citizenship United States

Post Office Address 4175 S. 1200 W., Hurricane, Utah 84737

Full name of third inventor	Gary B. Mosser
Inventor's Signature	
Date	
Residence	Tabernacle, New Jersey
Citizenship	United States
Post Office Address	5 Colonial Court, Tabernacle, New Jersey 08088

Full name of fourth inventor	Michael J. Fevola
Inventor's Signature	
Date	
Residence	Belle Mead, New Jersey
Citizenship	United States
Post Office Address	409 Township Line Road, Belle Mead, New Jersey 08502

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
16/262,898	01/30/2019		3980	I0113-198U1	41	3

CONFIRMATION NO. 3410

FILING RECEIPT

159443
Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

OC000000105985289

Date Mailed: 02/19/2019

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Rocco V. Burgo, Mullica Hill, NJ;
Michael E. Wright, Hurricane, UT;
Gary B. Mosser, Tabernacle, NJ;
Michael J. Fevola, Belle Mead, NJ;

Applicant(s)

Inolex Investment Corporation, Wilmington, DE

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 62/623,985 01/30/2018

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 02/15/2019

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 16/262,898**

Projected Publication Date: To Be Determined - pending completion of Corrected Papers

Non-Publication Request: No

Early Publication Request: No
Title

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 16/262,898

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	660
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	41 minus 20 =	* 21			OR	x 100 =	2100
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	3820

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1

CONFIRMATION NO. 3410

159443
Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

FORMALITIES LETTER

OC000000105965290

Date Mailed: 02/19/2019

NOTICE TO FILE CORRECTED APPLICATION PAPERS

Filing Date Granted

An application number and filing date have been accorded to this application. The application is informal since it does not comply with the regulations for the reason(s) indicated below. Applicant is given TWO MONTHS from the date of this Notice within which to correct the informalities indicated below. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

The required item(s) identified below must be timely submitted to avoid abandonment:

- Replacement drawings in compliance with 37 CFR 1.84 and 37 CFR 1.121(d) are required. The drawings submitted are not acceptable because:
  - Numbers, letters, and reference characters on the drawings must measure at least 0.32 cm (1/8 inch) in height. See Figure(s) 3-4.

Applicant is cautioned that correction of the above items may cause the specification and drawings page count to exceed 100 pages. If the specification and drawings exceed 100 pages, applicant will need to submit the required application size fee.

Items Required To Avoid Processing Delays:

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

- A properly executed inventor's oath or declaration has not been received for the following inventor(s):
  Rocco V. Burgo
  Michael E. Wright
  Gary B. Mosser
  Michael J. Fevola

Replies must be received in the USPTO within the set time period or must include a proper Certificate of Mailing or Transmission under 37 CFR 1.8 with a mailing or transmission date within the set time period. For more information and a suggested format, see Form PTO/SB/92 and MPEP 512.

Replies should be mailed to:

Mail Stop Missing Parts
Commissioner for Patents
P.O. Box 1450
Alexandria VA 22313-1450

Registered users of EFS-Web may alternatively submit their reply to this notice via EFS-Web, including a copy of this Notice and selecting the document description "Applicant response to Pre-Exam Formalities Notice". https://sportal.uspto.gov/authenticate/AuthenticateUserLocalEPF.html

For more information about EFS-Web please call the USPTO Electronic Business Center at 1-866-217-9197 or visit our website at http://www.uspto.gov/ebc.

If you are not using EFS-Web to submit your reply, you must include a copy of this notice.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/thaile/

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Non-Provisional Patent Application of: Inolex Investment Corporation			
Conf. No.:	3410	Group Art Unit:	Not Yet Assigned
Appln. No.:	16/262,898	Examiner:	
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making The Same		

AUTHORIZATION OF PAYMENT OF ALL EXTENSION OF TIME FEES

In the event that a Petition for Extension of Time is required at any time during the prosecution of the above-captioned application, but not submitted, the Commissioner is hereby authorized to charge any extension fee under 37 C.F.R. § 1.136(a) to Deposit Account No. 60-2689 (Billing No. I0113.0223).

Respectfully submitted,

Inolex Investment Corporation

8 March 2019 (Date)

By:

KRISTYNE A. BULLOCK
Registration No. 42,371
CALDERONE BULLOCK LLC
Two Greentree Centre
9000 Lincoln Drive East, Suite 301
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Telephone: (856) 446-6047
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Facsimile: (856) 267-5370
E-Mail: kbullock@calderonebullock.com

KAB/jxv

Electronic Acknowledgement Receipt

EFS ID:	35369837
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	159443
Filer:	Kristyne Alison Bullock
Filer Authorized By:	
Attorney Docket Number:	I0113-198U1
Receipt Date:	08-MAR-2019
Filing Date:	30-JAN-2019
Time Stamp:	18:35:46
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Authorization for Extension of Time all replies	198U1.pdf	45574 5cf5a352cc8b0de5236854960154e30396ce6002	no	1

Warnings:

Information:	
Total Files Size (in bytes):	45574

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

SCORE Placeholder Sheet for IFW Content

Application Number: 16262898 Document Date: 04/25/2019

The presence of this form in the IFW record indicates that the following document type was received in electronic format on the date identified above. This content is stored in the SCORE database.

Since this was an electronic submission, there is no physical artifact folder, no artifact folder is recorded in PALM, and no paper documents or physical media exist. The TIFF images in the IFW record were created from the original documents that are stored in SCORE.

- Drawing

At the time of document entry (noted above):

- USPTO employees may access SCORE content via DAV or via the SCORE web page.
- External customers may access SCORE content via PAIR using the Supplemental Content tab.

FILED ELECTRONICALLY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Patent Applications of:
Inolex Investment Corporation
103 Springer Building
411 Silverside Road
Wilmington, DE 19810

POWER OF ATTORNEY TO PROSECUTE APPLICATIONS BEFORE THE U.S. PATENT AND TRADEMARK OFFICE

Inolex Investment Corporation, assignee of the above application, by its undersigned representative, hereby revokes all previous powers of attorney given in the application identified in the enclosed Statement Under 37 C.F.R. §3.73(c).

Inolex Investment Corporation, by its undersigned representative, hereby appoints the registered attorneys and agents associated with Customer No. 159443, Calderone Bullock LLC, as its attorneys or agents to represent the assignee before the United States Patent and Trademark Office (U.S. PTO) in connection with any and all patent applications assigned only to the undersigned according to the U.S. PTO assignment records or assignment documents attached to this form and/or to the enclosed Statement Under 37 C.F.R. §3.73(c) and in accordance therewith, with full power of substitution and revocation, to prosecute the application identified in the enclosed Statement Under 37 C.F.R. § 3.73(c) and to transact all business in the U.S. PTO connected therewith.

Please change the correspondence address for the application identified in the enclosed Statement Under 3.73(c) to the address associated with **Customer No. 159443, namely, CALDERONE BULLOCK LLC**, Two Greentree Centre, 9000 Lincoln Drive East, Marlton New Jersey 08053. Please direct all communications and telephone calls to Lynda Calderone at (856) 446-6045 (telephone) or (856) 267-5370 (facsimile).

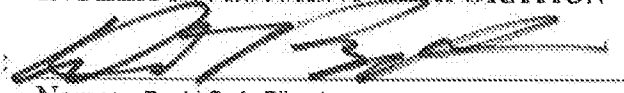
The undersigned states that he/she is authorized to sign the document on behalf of the assignee of the above application, and he/she certifies that, to the best of assignee's knowledge

and belief, title to the above application is in assignee by virtue of the documents provided and/or referenced in the enclosed Statement Under 37 C.F.R. §3.73(c).

Respectfully submitted,

INOLEX INVESTMENT CORPORATION

February 6, 2019
Date

By: 

Name: David C. A. Plimpton
Title: CEO
Telephone: 215-320-1507

ELECTRONICALLY FILED

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Patent Application of: Inolex Investment Corporation			
		Group Art Unit:	
Conf. No.:	3410		
Appln. No.:	16/262,898	Examiner:	
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1

Title: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making The Same.

STATEMENT UNDER 37 C.F.R. § 3.73(c)

3.73 (c) Statement:

Assignee, Inolex Investment Corporation, is owner of the entire right, title and interest in and to the above-referenced application and its related applications by virtue of: (a) the chain of title noted below wherein the documents are recorded as noted under 37 C.F.R. 3.73(c)(1)(ii) and in the Appointment of Attorney filed simultaneously herewith; or (b) the enclosed copies of the documentary evidence of the chain of title set forth below and in the Appointment of Attorney that, as required under 3.73(c)(1)(i), were submitted for recordation or are being concurrently submitted for recordation pursuant to 37 C.F.R. 11.

Inolex Investment Corporation is the owner by virtue of and as set forth in the Appointment of Attorney by Assignee filed simultaneously herewith:

[X] An assignment from the inventors of the above-identified patent application dated February 8, 2019, February 15, 2019, February 19, 2019 and February 21, 2019. The assignment was recorded in the United States Patent and Trademark Office (PTO) on April 2, 2019 at Reel 048761, beginning at Frame 0016.

Respectfully submitted,

INOLEX INVESTMENT CORPORATION

4/24/19 By: _____

Lynda E. Calderone, Managing Member
and Attorney for Assignee
Registration No. 35,837
Two Greentree Centre
9000 Lincoln Drive East, Suite 301
Marlton, NJ 08053
Telephone: 856-446-6047
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Facsimile: 856-267-5370
E-Mail: lcalderone@calderonebullock.com

LLC/jxv
Enclosures
[X] Customer Number or Bar Code Label: **159443**

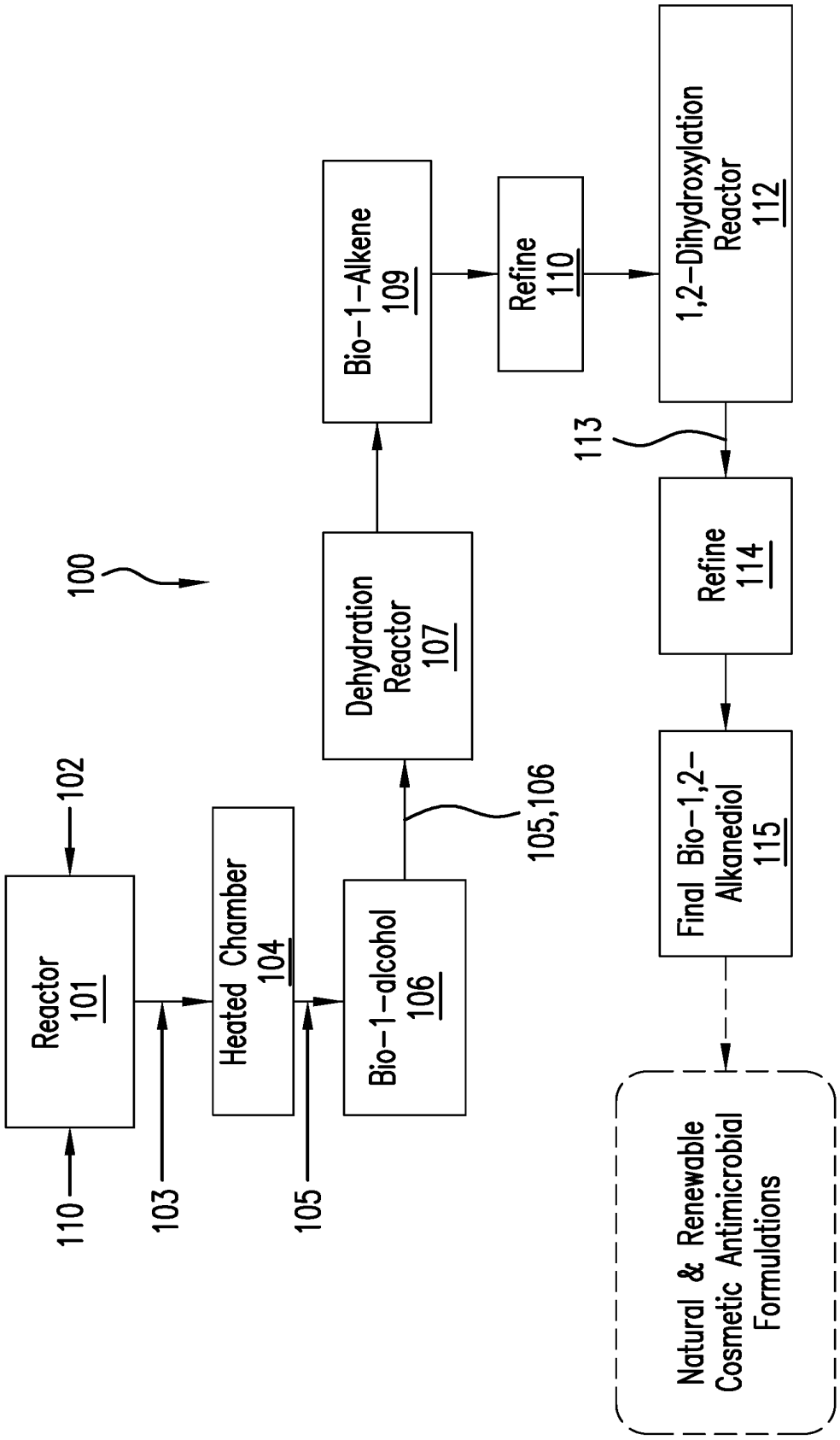
Reactor 101
Heated Chamber 104
Bio-1-alcohol 106
Dehydration Reactor 107
Bio-1-Alkene 109
Refine 110
1,2-Dihydroxylation Reactor 112
Refine 114
Final Bio-1,2-Alkanediol 115
Natural & Renewable Cosmetic Antimicrobial Formulations
100
102
110
103
105
105,106
113

FIG. 1

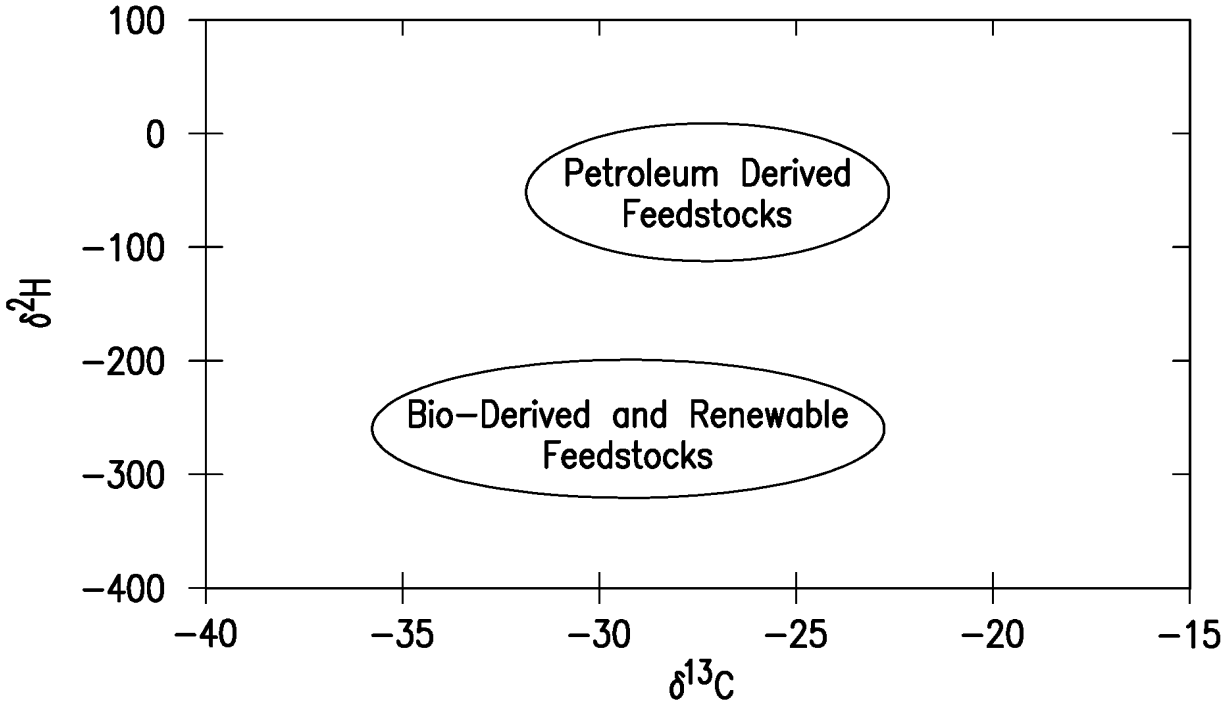
100
0
−100
−200
−300
−400
δ^2H
Petroleum Derived Feedstocks
Bio−Derived and Renewable Feedstocks
−40
−35
−30
−25
−20
−15
$\delta^{13}C$

FIG.2

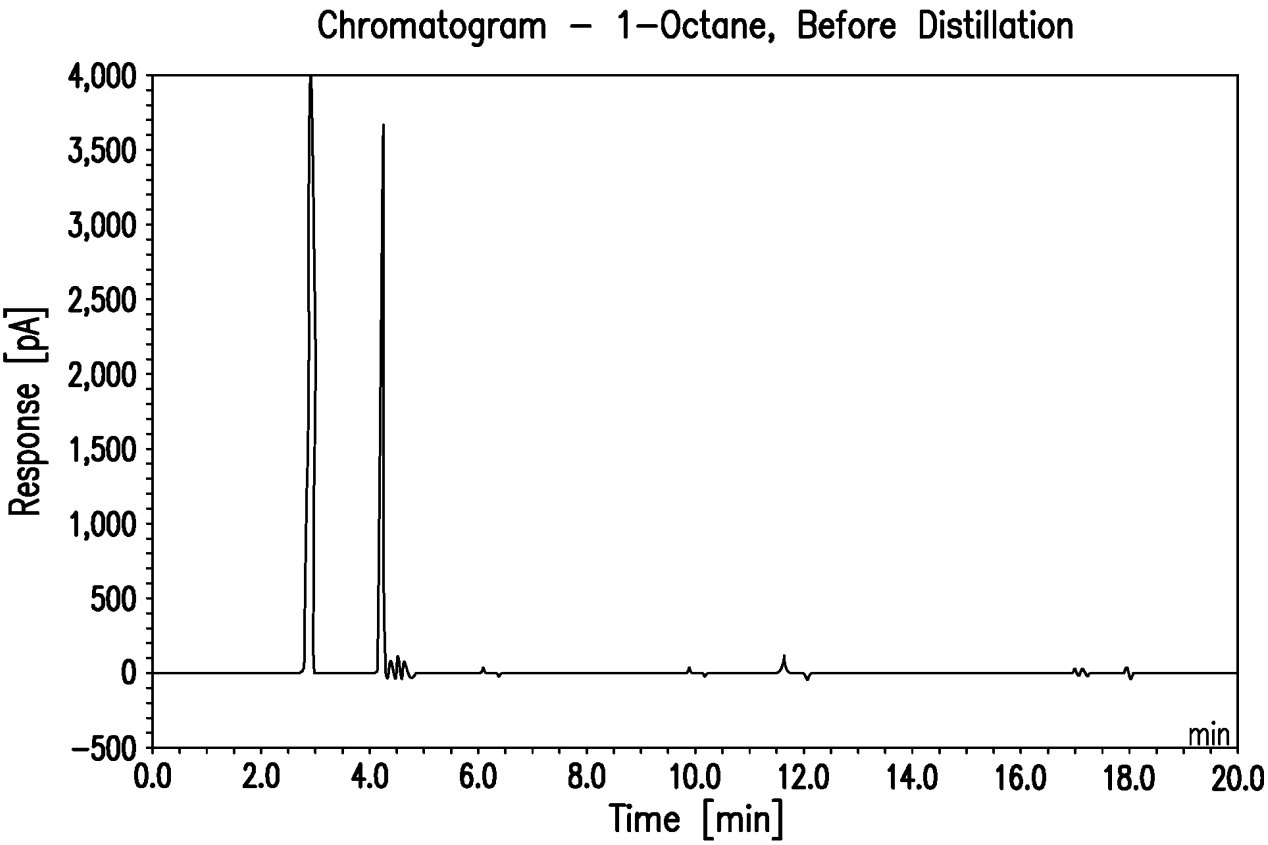
Chromatogram – 1–Octane, Before Distillation
Response [pA]
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
−500
min
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
Time [min]

FIG.3

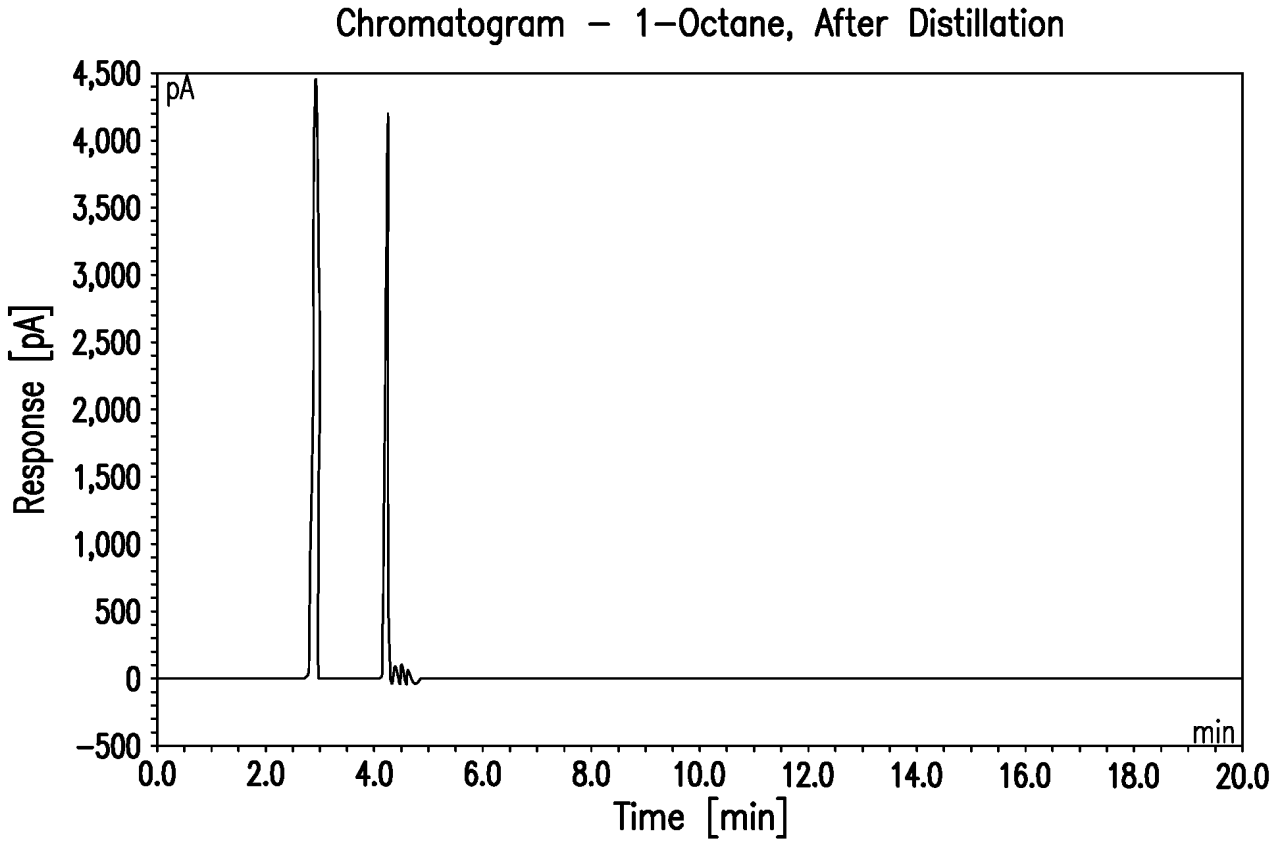
Chromatogram – 1–Octane, After Distillation
pA
Response [pA]
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
–500
min
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
Time [min]

FIG.4

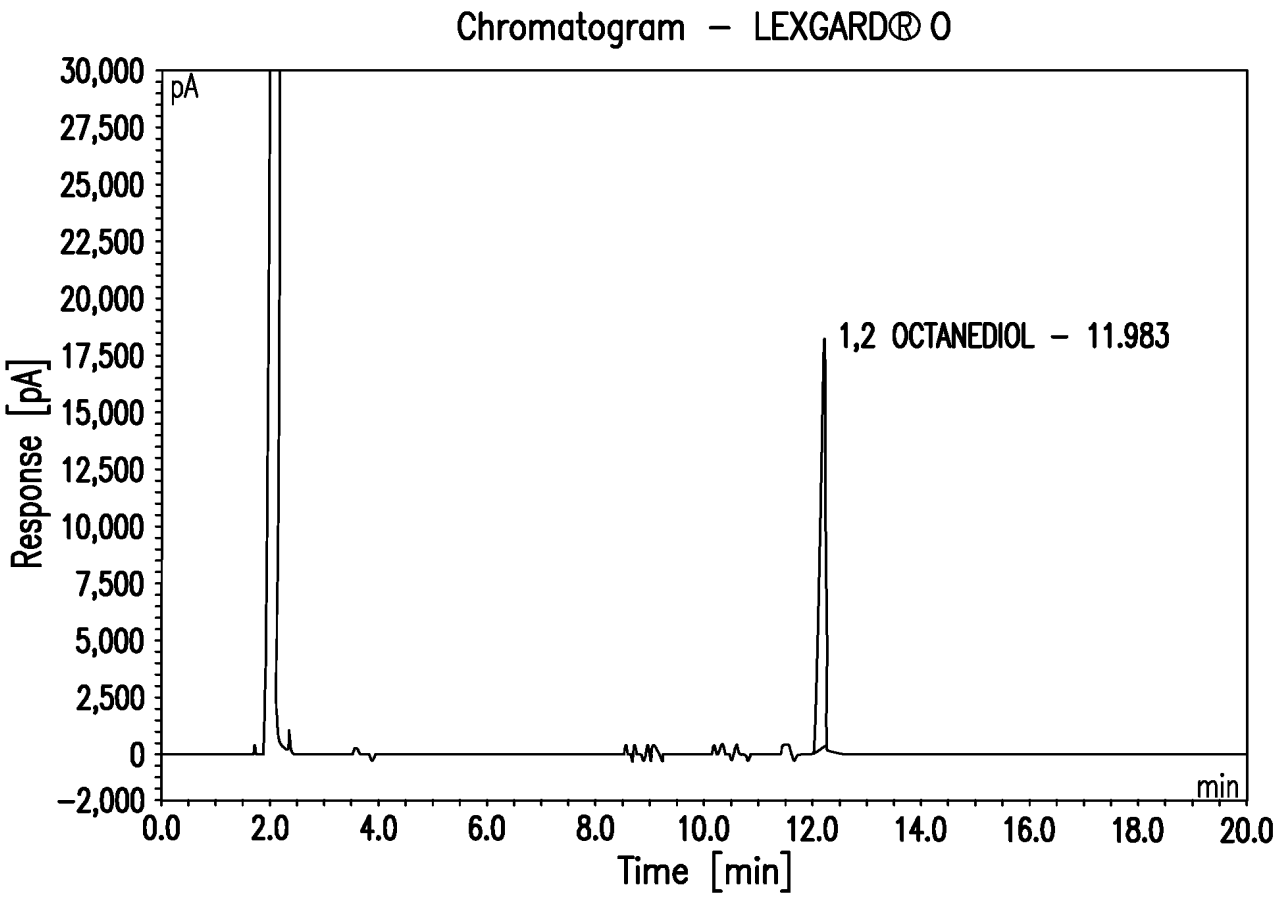
Chromatogram – LEXGARD® O
pA
1,2 OCTANEDIOL – 11.983
min
Response [pA]
Time [min]
30,000
27,500
25,000
22,500
20,000
17,500
15,000
12,500
10,000
7,500
5,000
2,500
0
−2,000
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0

FIG.5

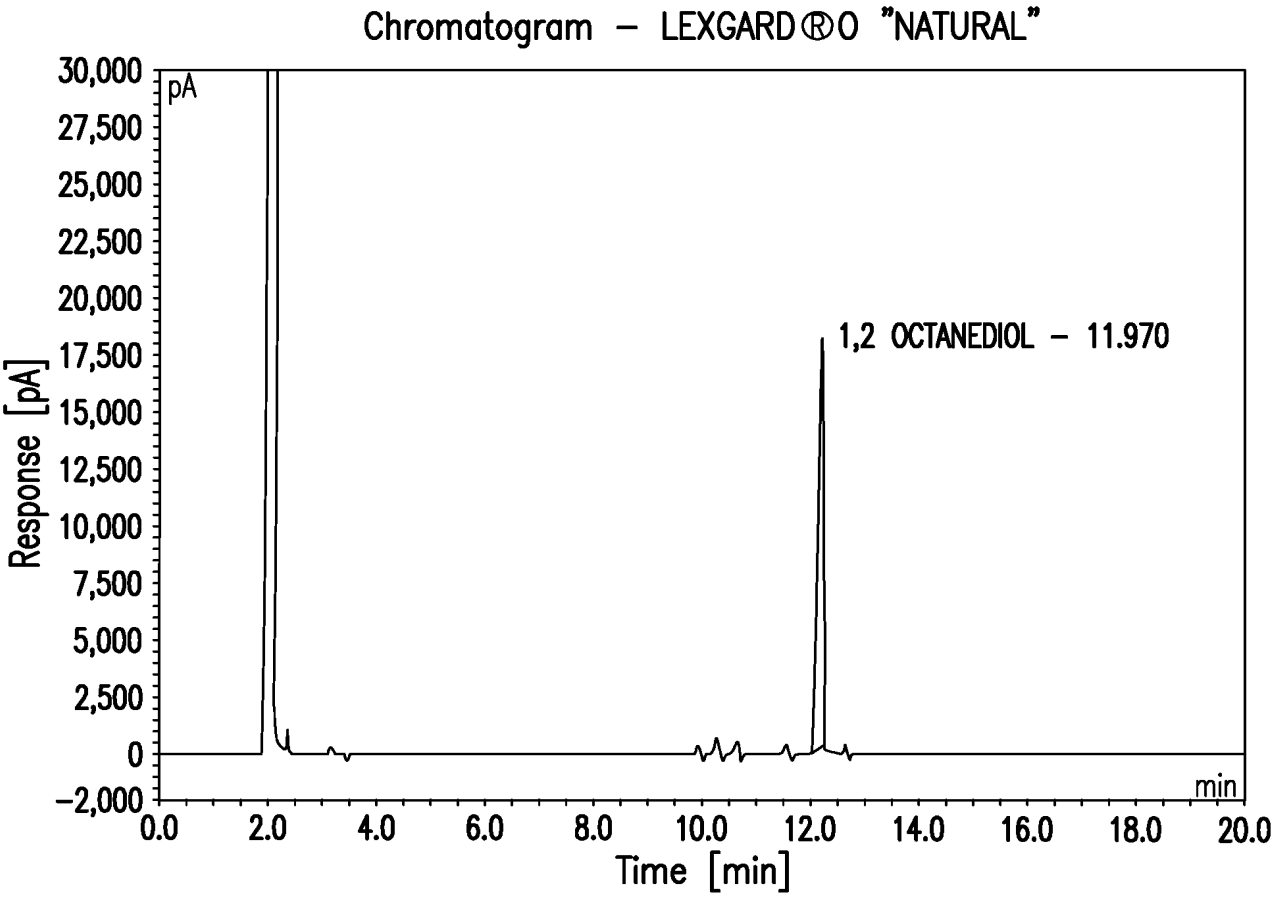
Chromatogram – LEXGARD®O "NATURAL"
pA
1,2 OCTANEDIOL – 11.970
min
Response [pA]
Time [min]
30,000
27,500
25,000
22,500
20,000
17,500
15,000
12,500
10,000
7,500
5,000
2,500
0
-2,000
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0

FIG.6

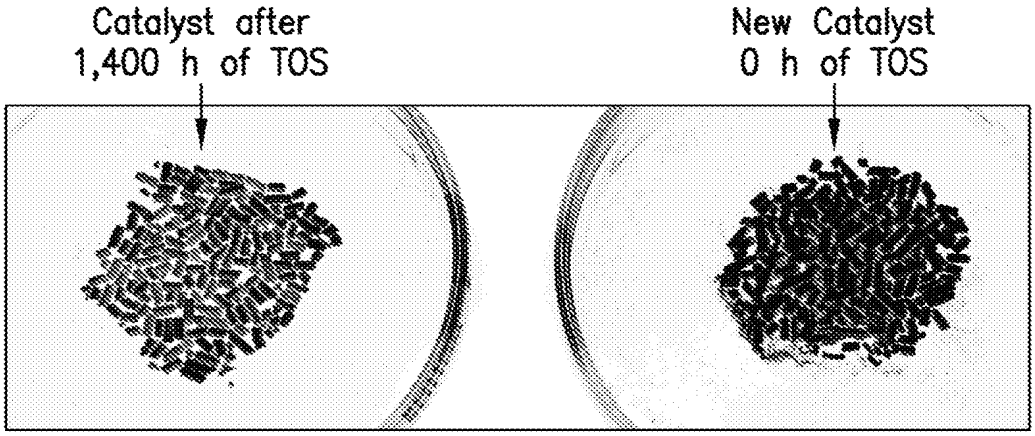

FIG. 7

Electronic Acknowledgement Receipt

EFS ID:	35828846
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	159443
Filer:	lynda Leigh Calderone
Filer Authorized By:	
Attorney Docket Number:	I0113-198U1
Receipt Date:	25-APR-2019
Filing Date:	30-JAN-2019
Time Stamp:	12:43:13
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	Transmittal.pdf	158571 89d8bc94face5e15c6d13e41c8e83b1482642c66	no	3

Warnings:

Information:					
2	Oath or Declaration filed	Declaration.pdf	119123 f7301ce4614761f07669c3db2eed921cc4312bab	no	3
Warnings:					
Information:					
3	Power of Attorney	poa.pdf	70177 0b63aac94e743b1e3955b7ba767feabe34eca356	no	2
Warnings:					
Information:					
4	Assignee showing of ownership per 37 CFR 3.73	373c.pdf	66248 85af1c3ab11c53a84f46463c542f5ddc8c70310d	no	2
Warnings:					
Information:					
5	Drawings-only black and white line drawings	Replacementdrawings.pdf	756525 e3c7eeea340767b5934a1743c264d1a6d04961ad	no	7
Warnings:					
Information:					
			Total Files Size (in bytes):	1170644	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

FILED ELECTRONICALLY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Patent Application of: Inolex Investment Corporation		
Conf. No.:	3410	Group Art Unit:
Appln. No.:	16/262,898	Examiner:
Filing Date.:	January 30, 2019	Attorney Docket No: I0113-198U1

Title: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

TRANSMITTAL OF DOCUMENTS

Enclosed are the following documents:

[X] [X] Inventors Declaration; [ ] Inventor(s) Declaration and Power of Attorney; [ ] Inventor(s) Oath; [ ] Substitute Statement

[ ] Appointment of Attorney by Applicant/Assignee.

[X] General Power of Attorney and 3.73(c) Statement

[ ] Revocation and Appointment of Attorney and Change of Correspondence Address.

[X] Replacement Drawings.

[ ] Substitute Application Data Sheet.

[ ] Verified English translation of application as filed.

[ ] Priority document(s): Certified copy(ies) of __ patent application No(s). __, filed in __ on __ from which priority is claimed under 35 U.S.C. § 119.

[ ] Microfiche computer program (Appendix).

[ ] Nucleotide and/or Amino Acid Sequence Submission, including:
[ ] Computer readable copy; [ ] Paper Copy; [ ] Verified Statement.

[ ] [ ] Formal drawings: _____ sheets; [ ] Replacement drawings: ____ sheets

[ ] Information Disclosure Statement, PTO/SB/08A or B and cited references.

[ ] Request for Refund.

[ ] Request for Corrected Filing Receipt. Attached is a marked-up copy of the Filing Receipt showing corrections.

[ ] Applicant(s), by its/their undersigned attorney, claim(s) Small Entity Status under 37 C.F.R. §1.27 as [ ] an Independent Inventor, or [ ] a Small Business Concern, or [ ] a Non-Profit Organization.

[ ] Micro Entity Status [ ] is hereby claimed by Applicant(s) and Micro Entity Certification is enclosed; [ ] has previously been claimed/established.

[ ] Preliminary Amendment. [ ] The application filing fees were paid upon filing and additional claim fees resulting from the Preliminary Amendment are calculated as follows:

					MICRO ENTITY		SMALL ENTITY		LARGE ENTITY	
	NO. OF CLAIMS AFTER AMEND.		HIGHEST NO. PREVIOUSLY PAID FOR	EXTRA	RATE	ADDIT. FEE	RATE	ADDIT. FEE	RATE	ADDIT. FEE
TOTAL		-			X $25	$	X $50	$	X $100	
INDEP.		-			X $115	$	X$230	$	X $460	
[ ] 1st PRESENTATION OF MULTIPLE DEPENDENT CLAIMS					$205		$410		$820	
					TOTAL	$	TOTAL	$	TOTAL	

[ ] Utility Non-Provisional Patent Application Filing Fees. The application filing fees were not paid at filing and are being paid herewith and are calculated as follows:

				MICRO ENTITY			SMALL ENTITY			LARGE ENTITY	
CLAIMS	NO. FILED		NO. EXTRA	BASIC FILING, SEARCH, AND EXAMINATION FEES:	$430		BASIC FILING, SEARCH, AND EXAMINATION FEES:	$ 785		BASIC FILING, SEARCH, AND EXAMINATION FEES:	$1,720
Total	@% -20 =		@%	X $ 25	$	OR	X $ 50	$	OR	X $100	$
Independent	@% - 3=		@%	X $115	$	OR	X $230	$	OR	X $460	$
[@%] Multiple Dependent Claims				X $205	$	OR	X $410	$	OR	X $820	$
[ ] Application Size Fee (if specification and drawings exceed 100 sheets)											
Total sheets	-100	Add'l sheets =	# of sets of 50 (round up to whole number) /50 =	X $100 =	$	OR	X $200 =	$	OR	X $400	$
Late Fee For Filing Fees, Inventor Oath or Declaration				$ 40	$	OR	$ 80	$	OR	$160	$

Late Fee For Non-English Specification	$ 35	$	OR	$ 70	$	OR	$140	$
	TOTAL	$	OR	TOTAL	$	OR	TOTAL	$

[ ] Other:

[ ] Applicant(s) herewith charge the following fees in the total amount of $_____ as calculated above to the credit card account, Calderone Bullock _____(Billing No. @%.@%):

[ ] Additional Claim Fees After Preliminary Amendment $_____.

[ ] Non-Provisional Utility Patent Application Filing Fees $_____.

[X] The Commissioner is hereby authorized to charge and/or credit Deposit Account No. 60-2689 (Billing No. I0113.0249) as noted below.

[X] Any overpayments or deficiencies in the above-calculated fees.

[X] Any additional fees required under 37 C.F.R. § 1.16 and § 1.17.

[X] In the event that a Petition for Extension of Time is required during the prosecution of this application, but not submitted, please charge any extension fee under 37 C.F.R. § 1.136(a) to our Deposit Account noted above.

Applicant believes there are no additional fees required with this submission. Should a fee be necessary, the Commissioner is hereby authorized to charge any fee or deficiency, or credit any overpayment to Deposit Account No. 60-2689 (Billing No. I0113-0249).

CORRESPONDENCE ADDRESS

4/25/19 By: _____

(Date)

LYNDA L. CALDERONE
Registration No. 35,837
CALDERONE BULLOCK LLC
Two Greentree Centre
9000 Lincoln Drive East, Suite 301
Marlton, NJ 08053
Telephone: 856-446-6047
Direct Dial: 856-446-6045
Facsimile: 856-267-5370
E-Mail: lcalderone@calderonebullock.com

[X] Customer Number or Bar Code Label: **000159443**

LLC/jxv
Enclosures

DECLARATION
(Original application)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original sole inventor (if only one name is listed below) or an original joint inventor (if plural names are listed below) of the subject matter that is claimed and for which a patent is sought on the invention entitled:

NATURAL 1,2-ALKANEDIOLS, COMPOSITIONS HAVING NATURAL 1,2-ALKANEDIOLS AND PROCESSES FOR MAKING THE SAME.

the specification of which is attached hereto and/or was filed on January 30, 3019 as Application No. 16/262,898.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to herein.

The above-identified application was made or was authorized to be made by me.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d), of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

FOREIGN PRIORITY APPLICATION(S)

			Priority Claimed
(Number)	(Country)	(Day/month/year filed)	[ ] Yes [ ] No
(Number)	(Country)	(Day/month/year filed)	[ ]Yes [ ] No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional patent application(s) listed below:

PROVISIONAL PRIORITY PATENT APPLICATION(S)

		Priority Claimed
62/623,985	January 30, 2018	[X] Yes [ ] No
(Application No.)	(Filing Date)	
		[ ] Yes [ ] No
(Application No.)	(Filing Date)	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements made in this Declaration are punishable under 18 U.S.C. §1001 by fine or imprisonment of not more than five (5) years.

Full name of first or sole inventor: Rocco V. Burgo

Inventor's Signature:

Date: 2/25/19

Residence: Mullica Hill, New Jersey

Citizenship: United States

Post Office Address: 604 Widgeon Court, Mullica Hill, New Jersey 08062

Full name of second inventor: Michael E. Wright

Inventor's Signature:

Date: Feb 15/2019

Residence: Hurricane, Utah

Citizenship: United States

Post Office Address: 4175 S. 1200 W., Hurricane, Utah 84737

Full name of third inventor	Gary B. Mosser
Inventor's Signature	Gary B Mosser
Date	2/21/19
Residence	Tabernacle, New Jersey
Citizenship	United States
Post Office Address	5 Colonial Court, Tabernacle, New Jersey 08088

Full name of fourth inventor	Michael J. Fevola
Inventor's Signature	Michael J. Fevola
Date	8 Feb 2019
Residence	Belle Mead, New Jersey
Citizenship	United States
Post Office Address	409 Township Line Road, Belle Mead, New Jersey 08502

Document code: WFEE

United States Patent and Trademark Office
Sales Receipt for Accounting Date: 05/01/2019

VVAN11 SALE #00000008 Mailroom Dt: 04/25/2019 602689 16262898
01 FC : 1251 200.00 DA

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 16/262,898

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	660
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	41 minus 20 =	* 21			OR	x 100 =	2100
INDEPENDENT CLAIMS (37 CFR 1.16(h))	3 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	3820

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
16/262,898	01/30/2019		3980	I0113-198U1	41	3

CONFIRMATION NO. 3410

UPDATED FILING RECEIPT

159443
Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

OC000000107835833

Date Mailed: 05/02/2019

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Rocco V. Burgo, Mullica Hill, NJ;
Michael E. Wright, Hurricane, UT;
Gary B. Mosser, Tabernacle, NJ;
Michael J. Fevola, Belle Mead, NJ;

Applicant(s)

Inolex Investment Corporation, Wilmington, DE

Power of Attorney: The patent practitioners associated with Customer Number 159443

Domestic Priority data as claimed by applicant

This appln claims benefit of 62/623,985 01/30/2018

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 02/15/2019

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 16/262,898**

Projected Publication Date: 08/08/2019

Non-Publication Request: No

Early Publication Request: No

Title

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

Preliminary Class

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific

countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1

CONFIRMATION NO. 3410

POA ACCEPTANCE LETTER

159443
Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

OC000000107754047

Date Mailed: 05/02/2019

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 04/25/2019.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/ebekele/

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United States Patent and Trademark Office
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

159443 7590 08/06/2019

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

EXAMINER	
CUTLIFF, YATE KAI RENE	

ART UNIT	PAPER NUMBER
1622	

NOTIFICATION DATE	DELIVERY MODE
08/06/2019	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

USP@calderonebullock.com

Office Action Summary	Application No. 16/262,898	Applicant(s) Burgo et al.	
	Examiner YATE K CUTLIFF	Art Unit 1622	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 1/30/2019.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-41 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-41 is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☑ The drawing(s) filed on 4/25/2019 is/are: a)☑ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☑ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Status of Claims

2. Claims 1 - 41 are pending.

Claims 42 - 87 have been canceled

Claims 1 - 41 are rejected.

Information Disclosure Statement

3. The listing of references in the specification is not a proper information disclosure statement. 37 CFR 1.98(b) requires a list of all patents, publications, or other information submitted for consideration by the Office, and MPEP § 609.04(a) states, "the list may not be incorporated into the specification but must be submitted in a separate paper." Therefore, unless the references have been cited by the examiner on form PTO-892, they have not been considered.

Claim Objections

4. Claim 40 is objected to because of the following informalities: The claim recites "The process according to claims 35, temperature during…". I appears that a word has been omitted before "temperature". Appropriate correction is required.

Claim Rejections - 35 USC § 112

5. Claims 1- 34 and 39 – 41 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and

distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

6. Claims 1 – 29 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being incomplete for omitting essential steps, such omission amounting to a gap between the steps. See MPEP § 2172.01. The omitted steps relate to the conversion of the bio-alkene to a bio 1,2-alkanediol. The disclosure and Example 7 reference the conversion requires the reaction of the 1-bio-alkene in the presence of formic acid or acetic acid, and a peroxide forming an intermediate solution. The intermediate solution is treated with sodium hydroxide and water for base hydrolysis in order to obtain the complete the formation of the 1,2-alkanediol. The disclosure at [0090] teaches that various known chemical reactions can be used that have known use when converting petro-alkanes to 1,2-alkanediols. However, Applicant's process, as taught in the disclosure, follows specific processing steps in order for the desired 1,2-alkanediol to be completely formed by their conversion process.

In the prior arts that after the initial reaction the intermediates can be subjected to various after treatments to obtain the finally desired 1,2-alkanediols. For instance in in Osterholt et al. (US 7,385,092), in a reaction of 1-alkene, the intermediates are subjected to acid catalyzed transesterification without additional base hydrolysis to obtain the final 1,2-alkanediol. A similar processing step is set out in the teachings of Swern but, the transesterification reaction is catalyzed with a base, without a hydrolysis follow-up. (Journal of the American Chemical Society, 1946, pp. 1506, Experimental left col.). Further, in the process of Osaka the reaction mixture containing the intermediates are subjected to acid catalyzed transesterification followed by treatment with an

aqueous solution of sodium hydroxide. The prior art teachings discussed above, wherein 1-alkene is converted to 1,2-alkanediol, disclose that where the initial reactants are formic acid and hydrogen peroxide an additional reaction step is needed before the possible use of hydrolysis in order to complete the formation of the diol. Thus, for these reasons, it is deemed that claim 1 has omitted the essential steps required to fully convert the bio 1-alkene.

7. Claims 2 – 29 are rejected for being dependent upon a rejected base claim.

8. Claims 30 - 34 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being incomplete for omitting essential steps, such omission amounting to a gap between the steps. See MPEP § 2172.01. The omitted steps relate to the conversion of the bio-alkene to a bio 1,2-alkanediol. The disclosure and Example 7 reference the conversion requires the reaction of the 1-bio-alkene in the presence of formic acid or acetic acid, and a peroxide forming an intermediate solution. The intermediate solution is treated with sodium hydroxide and water for base hydrolysis in order to obtain the complete the formation of the 1,2-alkanediol. The disclosure at [0090] teaches that various known chemical reactions can be used that have known use when converting petro-alkanes to 1,2-alkanediols. However, Applicant's process, as taught in the disclosure, follows specific processing steps in order for the desired 1,2-alkanediol to be completely formed by their conversion process.

9. Applicant is directed to paragraph 5 for the full discussion of the Examiner's basis for the rejection.

10. Claims 31 – 34 are rejected for being dependent upon a rejected base claim.

Claim Rejections - 35 USC § 112

11. Claim 39 recites the limitation "The process according to claim 38" in line 1. There is insufficient antecedent basis for this limitation in the claim. It is suggested that "process" be deleted and replaced with –method--.

12. Claim 40 recites the limitation "The process according to claim 35" in line 1. There is insufficient antecedent basis for this limitation in the claim. It is suggested that "process" be deleted and replaced with –method--.

13. Claim 41 recites the limitation "The process according to claim 40" in line 1. There is insufficient antecedent basis for this limitation in the claim. It is suggested that "process" be deleted and replaced with –method--.

Claim Rejections - 35 USC § 103

14. In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

15. This application currently names joint inventors. In considering patentability of the claims the examiner presumes that the subject matter of the various claims was commonly owned as of the effective filing date of the claimed invention(s) absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and effective filing dates of each claim that was not commonly owned as of the effective filing date of the later invention in order for the examiner to

consider the applicability of 35 U.S.C. 102(b)(2)(C) for any potential 35 U.S.C. 102(a)(2) prior art against the later invention.

16. The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

17. The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103 are summarized as follows:

1. Determining the scope and contents of the prior art.

2. Ascertaining the differences between the prior art and the claims at issue.

3. Resolving the level of ordinary skill in the pertinent art.

4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

18. Claims 35 – 41 are rejected under 35 U.S.C. 103 as being unpatentable over Wright et al. (WO2016/007196).

19. The rejected claims cover, inter alia, a method for treating a catalyst for use in dehydration of alcohols, comprising: providing a y-alumina catalyst; treating the y-alumina catalyst with a base comprising a Group I or a Group II metal; and heating the y-alumina catalyst to a temperature of about 400°C to about 500°C.

20. Dependent claims 36 – 39 further limit the reactants. Dependent claims 40 – 41 further limit the method.

21. However, Wright discloses a method for treating catalyst for use in the dehydration of alcohols to diene products. ([22] & [32]). In the teachings of Wright a gamma-alumina catalyst is provided. The gamma-alumina catalyst is treated with a base comprising a Group 1 or Group 2 metal. ([33] – [34]). Calcination of the catalyst can be carried out at temperatures of about 100°C to about 900°C. ([122]). In Wright the base comprises calcium. ([33]). Also, in Wright the calcium base is a promoter and heating is conducted during calcination. ([122]). Further, the Ca-modified catalyst comprised about 0.8wt-% to about 4.0 wt.-% or about 1.0 wt.-% to 1.7 wt.-% of the total catalyst (weight of Ca^{+2}/(weight of inorganic support + weight of Ca^{+2}) (consistent with 1.1 – 5.6 weight percent based on the weight of CaO, provided the molar mas of Ca is 40g/mol; and Cao is 56g/mol) . ([122]). The temperature during calcination is about 100°C to about 900°C.

The difference between Wright and the claimed inventions is that they do not teach the invention with particularity so as to amount to anticipation (See M.P.E.P. § 2131: "[t]he identical invention must be shown in as complete detail as is contained in the ... claim." Richardson v. Suzuki Motor Co., 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989). The elements must be arranged as required by the claim, but this is not an ipsissimis verbis test, i.e., identity of terminology is not required. In re Bond, 910 F.2d 831, 15 USPQ2d 1566 (Fed. Cir. 1990)).

However, based on the above, Wright teaches the elements of the claimed invention with sufficient guidance, particularity, and with a reasonable expectation of success, that the invention would be prima facie obvious to one of ordinary skill before the effective filing date of the claimed invention (the prior art reference teaches or

suggests all the claim limitations with a reasonable expectation of success. See M.P.E.P. § 2143).

Art Made of Record

22. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. U.S. 8,912,373 (Wright, M. E.)

Conclusion

23. Any inquiry concerning this communication or earlier communications from the examiner should be directed to YATE K. CUTLIFF whose telephone number is (571)272-9067. The examiner can normally be reached on Monday-Friday (8:30 - 5:30).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf can be reached on (571) 272 - 2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should

you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

Notice of References Cited	Application/Control No. 16/262,898	Applicant(s)/Patent Under Reexamination Burgo et al.	
	Examiner YATE K CUTLIFF	Art Unit 1622	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-7385092-B2	06-2008	Osterholt; Clemens	A61K8/345	568/858
*	B	US-8912373-B2	12-2014	Wright; Michael E.	B01J37/06	585/16
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N	WO-2016007196-A1	01-2016	WO	Michael E. Wright	C10G45/32
	O	JP-2008007463-A	01-2008	JP	YAMAMOTO, TATSURO	C07C 29/128
	P	CN-104926600-A	09-2015	CN	HU XUEYI et al.	C07C 29/03
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Swern, D. et al., Hydroxylation and Epoxidation of some 1-olefins with per-acids, 1946, Journal of the American Chemical Society, vol. 68, pp. 1504 - 1507 (Year: 1946)
	V	JP 2008-007463, Osaka Organic Chem IND, Method for producing 1,2-Alkanediol, 2008, English translation 16 pages (Year: 2008)
	W	CN 104926600, FOSHAN DEPINT ADVANCED MATERIALS CO LTD, Method for synthesizing 1,2-pentanediol by one-pot method, 2015, English translation, 11 pages (Year: 2015)
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/01/2019								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
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	35	✓								
	36	✓								
	37	✓								
	38	✓								
	39	✓								
	40	✓								
	41	✓								

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC - Searched*		
Symbol	Date	Examiner
C07C 29/04	08/01/2019	ykc
C07C 31/20	08/01/2019	ykc
C07C 33/025	08/01/2019	ykc
C07C 2521/04	08/01/2019	ykc
B01J 21/04	08/01/2019	ykc
B01J 23/06	08/01/2019	ykc
B01J 37/08	08/01/2019	ykc

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

Search Notes		
Search Notes	**Date**	**Examiner**
Palm Inventor Search	08/01/2019	ykc
East	08/01/2019	ykc
C07C 29/04	08/01/2019	ykc
C07C 31/20	08/01/2019	ykc
C07C 33/025	08/01/2019	ykc
C07C 2521/04	08/01/2019	ykc
B01J 21/04	08/01/2019	ykc
B01J 23/06	08/01/2019	ykc
B01J 37/08	08/01/2019	ykc

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**

(19)中华人民共和国国家知识产权局

(12)发明专利申请

(10)申请公布号 CN 104926600 A
(43)申请公布日 2015.09.23

(21)申请号 201510239573.4

(22)申请日 2015.05.12

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(51)Int.Cl.
C07C 29/03(2006.01)
C07C 31/20(2006.01)

权利要求书1页 说明书8页 附图1页

(54)发明名称

一种一锅法合成1,2-戊二醇的方法

(57)摘要

本发明涉及一种低温条件下由正戊烯为原料一锅法高产率合成1,2-戊二醇的方法。本发明的反应温度低,降低了1-戊烯原料高温挥发而导致泄露风险,同时降低了对设备耐压需求;采用多步一锅法工艺缩短了工艺流程;反应中不采用有腐蚀、有污染和有害化合物为原料,消除传统工艺采用原料多倍量的有机酸载氧剂,该工艺的环境友好性佳;本发明的原料来源广泛,生产成本低,经济性好。

CN 104926600 A

1. 一种一锅法合成1,2-戊二醇的方法，其特征在于以1-戊烯、双氧水、催化剂在溶剂中加热到一定的温度反应下反应一定时间。

2. 权利1所述的双氧水，其特征在于过氧化氢浓度为10%-80%（W/W）。

3. 权利1或权利2所述的1-戊烯与过氧化氢的物质量比，其特征在于比值为1:1-2。

4. 权利1所述的催化剂，其特征在于催化剂为四氯化钛，或具有$Ti(OR)_4$通式的钛酸酯，R为C_1-C_{10}的烷基。

5. 权利1 或权利4所述的催化剂，其特征在于加入量为原料1-戊烯质量的0.1%-10%（W/W）。

6. 权利1所述的反应温度，其特征为范围为10 ℃-100℃。

7. 权利1或权利6所述的反应温度，其特征为恒温反应。

8. 权利1或权利6所述的反应温度，其特征在于程序升温反应。

9. 权利1所述的反应时间为1h-24h。

10. 权利1所述的溶剂，其特征在于溶剂为甲醇、乙醇、异丙醇、正丁醇、丙酮、甲乙酮、二丁酮中的一种或几种的混合物。

一种一锅法合成 1,2-戊二醇的方法

技术领域

[0001] 本发明涉及一种一锅法合成 1,2- 戊二醇的方法，属于有机化合物合成领域。

背景技术

[0002] 1,2- 戊二醇是合成高效、低毒和活性谱广的丙环唑类杀菌剂（比利时杨森医药集团[1]开发，已在多国获登记）的重要中间体，用于构建丙环唑分子的缩酮结构[2]。1,2- 戊二醇还具有保湿功能，与其它保湿剂复配使用产生较强的协同效应[3]，可用作化妆品或个人护理用品[3-4]的保湿功效成分。1,2- 戊二醇还具有抑菌性[5]，在不添加其它防腐剂的配方中亦可有效抑制产品的变质[6]。

[0003] 1,2- 戊二醇的合成方法主要以下两种：(1) 正戊烯环氧化反应和后继的水解反应；(2)糠醛或糠醇的加氢还原。第一种方法主要存在生产安全和污染大等不足；第二种方法主要存在原料转化率不高、副反应多和产品提纯困难等不足；具体情况见如下分析。

[0004] 德固赛公司[7]公开了以正戊烯为原料、苯为溶剂、丙酸为载氧剂和氢氧化钠为开环试剂的连续相中合成 1,2- 戊二醇的方法。Ciba-Geigy 公司公开了一种采用正戊烯和甲酸为原料，过氧化氢为氧化剂，氢氧化钠为开环试剂的合成 1,2- 戊二醇连续生产工艺[8]。浙江联盛集团[9]和中国石化[10]也公开了以正戊烯、甲酸和过氧化氢为原料的类似工艺。该工艺原料沸点低（正戊烯的沸点 30.1℃），易因低沸点有机化合物挥发导致的劳动者安全和生产安全等隐患；以甲酸为原料对设备的腐蚀性强，少量泄露的甲酸对操作者的皮肤有强腐蚀作用，同时以正戊烯物质的量 2-10 倍甲酸导致大量液体有机废弃物待处理；该反应的副产物多，产品的分离纯化相对困难。大连化物所[11]公开了以磷钨酸催化正戊烯与过氧化氢反应直接制备 1,2- 脂肪二醇的方法，解决了因用过量甲酸引起的一系列问题；但仍旧不能解决在反应条件下低沸点原料挥发和对设备耐压要求高等不足。中科院煤炭所朱玉雷[12]报道了合成 1,2- 戊二醇的绿色化学新途径，以二氧化锰负载贵金属钌催化糠醇加氢合成 1,2- 戊二醇。该方法中应用了贵金属钌，价格昂贵；同时催化剂的载体二氧化锰并不是特别适用于工业应用的载体材料。天津医科大学侯薇[13]报道了正戊烯为原料，硼酸钠为氧化剂，醋酸酐为反应溶剂和反应物合成了乙酸单戊二醇酯，该酯类化合物在碱性条件下进一步水解得 1,2- 戊二醇。该方法避免了甲酸等腐蚀性强的化合物。但是过量醋酸酐和氧化剂导致反应产品后处理困难；正戊烯与醋酸酐化学计量比反应生成乙酸单戊二醇酯，消耗了大量的乙酸酐，增加了原料成本；氧化反应形成单酯与水解反应的分离，延长了反应路线，增加了操作成本。Severeyns 等[14]以 NMO 和四氧化锇催化剂的作用下催化正戊烯的双羟基化反应合成 1,2- 戊二醇应的二醇。该方法使用的四氧化锇催化剂毒性高、价格昂贵、受热易产生有毒气体，因此该路线的工业应用价值极微。

[0005] 早在 1931 年，Adkins[15]报道了亚铬酸铜催化糠醇加氢合成了 1,2- 戊二醇和 1,5- 戊二醇的混合物，0.75mol 糠醇中加入 3g 催化剂，在 175℃下反应 11 小时，1,2- 戊二醇和 1,5 戊二醇的总产率最高达到 70%。但是 Manly 在 1958 年[16]采用 Adkins 相似的条件反应，1,2- 戊二醇的收率却仅仅为 4.4%。日本筑波大学的 Tomishige[17]在 Chem Comm 上发表了

金属负载的钌和铼催化糠醇的加氢还原反应，结果产物中未检测到1,2-戊二醇，而是选择性的生成了1,5-戊二醇。浙江大学许彦娟[18]研究了Cu-Zn、Cu-Mn、Cu-Cr、Raney Cu、Raney Ni及贵金属负载型催化剂Pt/C、Pd/C、Ru/ AI2O3等催化糠醇选择性加氢还原为1,2-戊二醇，其中Cu-Zn的催化性能最优。在反应温为150~160 ℃, 反应压力7~8MPa, 反应时间10 h下，糠醇转化率达到69.2%，1,2-戊二醇的选择性达到46.2 %, 其收率达到32.0%。原料转化率低、副反应多和1,2-戊二醇的收率低仍旧是该路线的致命缺陷。赢创工业集团[19]公开了糠醇加氢还原合成1,2-戊二醇的方法。珠海凯美科技有限公司[20]公开了非贵金属催化剂选择性加氢合成1,2-戊二醇。该方法利用农副产品深加工产物糠醛为原料，大大解决了受正戊烯原料限制等问题；该方法采用氧化铜等非贵金属催化剂催化加氢，解决了贵金属催化剂价格昂贵和回收困难等问题；但是该方法仍旧存在原料转化不完全，副反应多和产率低等问题，由此带来了分离困难、产品纯度不高和反应路线非环境友好等新问题；氧化铜催化加氢的性能差，导致加氢反应的压力过高，由此带来生产过程中的安全隐患。日本仙台紧凑型化工研究中心的Maya Chatterjee[21]报道了在超临界二氧化碳中催化四氢糠醇合成1,2-戊二醇，其中Pd/MCM-41为催化剂的1,2-戊二醇得率最高，达到77.4%，还含有12.6%的1,5-戊二醇和10%的1-戊醇和2-戊醇的混合物。该方法虽然提高了1,2-戊二醇的收率，但是仍旧采用负载型贵金属为催化剂，操作成本相对较高；采用超临界二氧化碳为溶剂，反应体系的压力也较大，该工艺也不适合于工业规模生产1,2-戊二醇。

[0006] 除了上述的两种方法外，还有一些零星报道合成1,2-戊二醇的方法。德固赛公司[22]公开了正丁醛与氢氰酸亲核反应生成邻羟基正戊腈，水解邻羟基正戊腈得到邻羟基正戊醇，再在贵金属钌和铼等非均相催化剂催化下合成1,2-戊二醇。该方法中原料氢氰酸为剧毒化学品，对操作者有潜在的致命性；反应分三步进行，路线长；第一步亲核反应因羟醛缩合等副反应使得反应控制困难，副产物多，产品提纯困难；使用贵金属钌和铼为催化剂，增加了生产成本。江苏扬农化工集团[23]公开了2-氯代戊醇在碱性溶剂中发生环氧化反应。该工艺虽可能高产率获得1,2-戊二醇，但2-氯代戊醇原料不易得，同时反应过程中常压蒸馏环氧戊烷尚存在操作不安全的致命隐患。江苏化工农药集团丁小兵在《安徽化工》报道了[24]用硼氢化钠还原邻羟基正戊酸合成1,2-戊二醇。硼氢化钠的价格昂贵和羟基正戊酸的不易得导致该工艺实现工业化生产困难重重。

[0007] 综上所述，已见文献报道的以正戊烯环氧化反应、环氧化合物开环反应合成1,2戊二醇的路线存在原料沸点低和挥发性强、该工艺产生的液体废弃物多、产品的分离和后处理困难等不足；已见文献报道的以糠醇或糠醛加氢还原反应合成1,2-戊二醇的路线虽然解决了原料来源问题，但仍旧存在贵金属催化剂价昂、原料转化率不高、产物选择性不佳和产品纯度低等不足；报道的其它方法或存在原料价昂、或原料来源不足、或反应过程中使用到剧毒化学品、或路线长、或反应困难、或产物提纯困难等不足。

[0008] [背景技术的参考文献]

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发明内容

[0009] ［要解决的问题］

本发明的目的在于提供一种在低温条件下由正戊烯为原料合成 1,2-戊二醇的方法。

[0010] 本发明的另一个目的在于提供一种对设备无腐蚀的原料合成 1,2-戊二醇的方法。

[0011] 本发明的另一个目的在于提供一种对环境更加友好的由 1-戊烯为原料合成 1,2-戊二醇的方法。

[0012] ［技术方案］

本发明所述的方法，包括以下步骤：

1 在反应釜中分别加入一定量溶剂和催化剂，并混合均匀；

2 在反应釜中再加入一定量正戊烯，并混合均匀；

3 保持反应釜内物料温度为0-40 ℃，并在慢速搅拌条件下缓慢滴加一定量双氧水，反应数小时；

4 在反应釜中加入一定量水或不加水；

5 在反应釜中加入一定量的二氧化锰；

6 将反应釜内温度上升至30-80 ℃，反应数小时；

7 反应结束后蒸发体系中的溶剂，过滤后得1,2-戊二醇粗产品；

8 上述粗产品经减压蒸馏后得含量大于99.5%的1,2-戊二醇。

[0013] ［有益效果］

与现有1,2-戊二醇的合成方法相比，本发明的有益效果如下：

1 本发明提供的反应温度为低热，降低了1-戊烯原料高温挥发而导致泄露风险和降低对设备耐压需求。

[0014] 2 本发明提供的多步一锅法反应工艺路线短，加工简便和产品产率高的工艺路线合成1,2-戊二醇。

[0015] 3 本发明的工艺过程无腐蚀、无污染、不产生任何有害化合物，因此本发明的合成工艺有较好的环境友好性佳。

[0016] 4 本发明方法的原料来源广泛且低廉，工艺路线短，生产成本低，经济性好。

附图说明

[0017] 图1 为1,2-戊二醇的溴化钾盐片涂膜法的傅立叶变换红外光谱图。图中3361cm^{-1}处为缔合羟基的伸缩振动吸收；2958 cm^{-1}，2931 cm^{-1}和2872 cm^{-1}处为甲基和亚甲基的碳氢伸缩振动的特征吸收。

[0018] 图2 为实施例2的产品1,2-戊二醇的气相色谱图。气相色谱条件为：OV1701毛细管柱、30m、0.32um，氮气为载气、柱前压0.1 MPa，柱温180℃。面积归一化百分含量为99.89%，以丙二醇为内标物的内标标准曲线法测定的含量为99.85%。

具体实施方式

[0019] 下面结合实施例对本发明作出进一步说明，但本发明不限于以下实施例。

[0020] 实施例1

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入20 mL甲醇和0.1 g 四氯化钛，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入10 g正戊烯；在10 ℃条件下，在30 min左右经恒压分液漏斗缓慢滴加15 g 30%的过氧化氢水溶液，滴加完毕后在10 ℃下继续搅拌6 h；然后向反应器中再加入20 g水，再在50 ℃下反应8 h；在反应器中加入0.1 g二氧化锰，蒸馏回收溶剂甲醇并除去水分，过滤得10.3 g 纯度为97.3%（气相色谱，1,2-丙二醇内标物的内标标准曲线法，）的1,2戊二醇粗产品。

[0021] 实施例2

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入20 mL甲

醇和 0.1 g 钛酸四甲酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 14 g 浓度为 50% 的过氧化氢水溶液，滴加完毕后在 10 ℃下继续搅拌 6 h；然后向反应器中再加入 30 g 水，再在 50 ℃下反应 8 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂甲醇并除去水分，过滤得 13.0 g 纯度为 97.4%（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品；经减压蒸馏，收集 5 mmHg 下 80 ℃左右的馏分，得 12.1 g 纯度为 99.6 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2- 戊二醇产品。

[0022] 实施例 3

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 20 mL 异丙醇和 1.0 g 钛酸四丁酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 40 g 浓度为 10% 的过氧化氢水溶液，滴加完毕后在 10 ℃下继续搅拌 8 h；将体系温度升高到 80 ℃，继续反应 8 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂异丙醇并除去水分，过滤得 12.4 g 纯度为 95.2%（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品。

[0023] 实施例 4

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 20 mL 异丙醇和 2.0 g 钛酸四异丙酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 20 g 浓度为 20 % 的过氧化氢水溶液，滴加完毕后在 10 ℃下继续搅拌 10 h；然后向反应器中再加入 20 g 水，再在 60 ℃下反应 5 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂异丙醇并除去水分，过滤得 13.2 g 纯度为 96.5 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品。

[0024] 实施例 5

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 20 mL 乙醇和 1.5 g 钛酸四己酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 8 g 浓度为 80 % 的过氧化氢水溶液，滴加完毕后在 40 ℃下继续搅拌 2 h；然后向反应器中再加入 20 g 水，再在 70 ℃下反应 4 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂乙醇并除去水分，过滤得 12.5 g 纯度为 95.3 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品；经减压蒸馏，收集 5 mmHg 下 80 ℃左右的馏分，得 11.2 g 纯度为 99.5 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2- 戊二醇产品。

[0025] 实施例 6

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 30 mL 丙酮和 1.0 g 钛酸四异己酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 20 g 浓度为 30 % 的过氧化氢水溶液，滴加完毕后在 20 ℃下继续搅拌 4h；然后向反应器中再加入 10 g 水，再在 40 ℃下反应 20 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂丙酮并除去水分，过滤得 12.7 g 纯度为 95.9 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品。

[0026] 实施例 7

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 20 mL 甲乙酮和 0.3 g 四氯化钛，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 12 g 浓度为 30 %的过氧化氢水溶液，滴加完毕后在 30 ℃下继续搅拌 2 h；然后向反应器中再加入 10 g 水，再在 50 ℃下反应 16 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂甲乙酮并除去水分，过滤得 11.2 g 纯度为 98.1 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品。

[0027] 实施例 8

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 20 mL 四氢呋喃和 0.2 g 钛酸四甲酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 15 g 浓度为 30 %的过氧化氢水溶液，滴加完毕后在 40 ℃下继续搅拌 1 h；然后向反应器中再加入 20 g 水，再在 50 ℃下反应 4 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂四氢呋喃并除去水分，过滤得 14.5 g 纯度为 98.3 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品；经减压蒸馏，收集 5 mmHg 下 80 ℃左右的馏分，得 13.5 g 纯度为 99.9 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2- 戊二醇产品。

[0028] 实施例 9

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 20 mL 二乙酮和 0.3 g 钛酸四乙酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 10 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 10 g 浓度为 50 %的过氧化氢水溶液，滴加完毕后在 20 ℃下继续搅拌 10 h；然后向反应器中再加入 20 g 水，再在 50 ℃下反应 4 h；在反应器中加入 0.1 g 二氧化锰，蒸馏回收溶剂四氢呋喃并除去水分，过滤得 13.7 g 纯度为 98.0 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品；经减压蒸馏，收集 5 mmHg 下 80 ℃左右的馏分，得 12.4 g 纯度为 99.7 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2- 戊二醇产品。

[0029] 实施例 10

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 200 mL 无水甲醇和 3.0 g 钛酸四甲酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 200 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 300 g 浓度为 30 %的过氧化氢水溶液，滴加完毕后在 10 ℃下继续搅拌 10 h；然后向反应器中再加入 200 g 水，再在 50 ℃下反应 14 h；在反应器中加入 1 g 二氧化锰，蒸馏回收溶剂甲醇并除去水分，过滤得 290.2 g 纯度为 98.1 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品；经减压蒸馏，收集 5 mmlg 下 80 ℃左右的馏分，得 281.0 g 纯度为 99.7 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2- 戊二醇产品。

[0030] 实施例 11

在具有加热、温控、磁力搅拌、恒压滴液和回流装置的常压反应器中分别加入 200 mL 四氢呋喃和 3.0 g 钛酸四甲酯，慢速搅拌使之混合均匀；在慢速搅拌条件下用恒压滴液漏斗滴加入 200 g 正戊烯；在 10 ℃条件下，在 30 min 左右经恒压分液漏斗缓慢滴加 150 g 浓

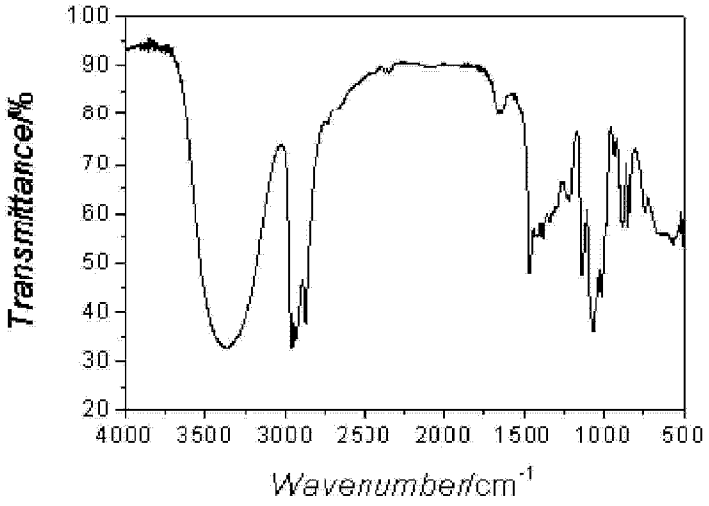
度为 50 % 的过氧化氢水溶液，滴加完毕后在 20 ℃下继续搅拌反应 10 h；然后向反应器中再加入 400 g 水，再在 50 ℃下反应 15 h；在反应器中加入 1 g 二氧化锰，蒸馏回收溶剂甲醇并除去水分，过滤得 292.0 g 纯度为 98.0 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品；经减压蒸馏，收集 5 mmHg 下 80 ℃左右的馏分，得 278.8 g 纯度为 99.7 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2- 戊二醇产品。

[0031] 实施例 12

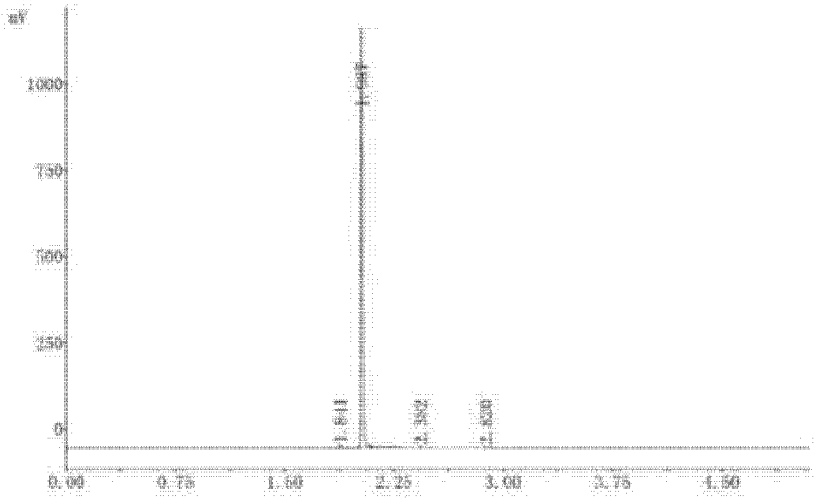
在具有加热、温控和机械搅拌的压热反应器中分别加入 200 mL 甲醇、3.0 g 钛酸四甲酯和 200 g 正戊烯；混合均匀后再加入 300 g 浓度为 30 % 的过氧化氢水溶液，然后在 60 ℃下继续搅拌反应 2 h；加入 400 g 水，再在 60 ℃下反应 10 h；将上述混合液转移到常压蒸馏装置中，蒸馏回收溶剂甲醇并除去水分，过滤得 150.2 g 纯度为 64.0 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品。

[0032] 实施例 13

在具有加热、温控和机械搅拌的压热反应器中分别加入 200 mL 四氢呋喃、3.0 g 钛酸四甲酯和 200 g 正戊烯；混合均匀后再加入 150 g 浓度为 50 % 的过氧化氢水溶液，然后在 80 ℃下继续搅拌反应 2 h；加入 400 g 水，再在 80 ℃下反应 10 h；将上述混合液转移到常压蒸馏装置中，蒸馏回收溶剂甲醇并除去水分，过滤得 120 g 纯度为 42.0 %（气相色谱，1,2- 丙二醇内标物的内标标准曲线法，）的 1,2 戊二醇粗产品。


Transmittance/%
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber/cm-1

附图 1


mV
1000
750
500
250
0
0.00
0.75
1.50
2.25
3.00
3.75
4.50

附图 2

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4H039 CA60 CA63 CE10 CH40

(54)【発明の名称】１，２－アルカンジオールの製造法

(57)【要約】
【課題】低臭気の１，２－アルカンジオールを高純度で容易かつ安全に製造しうる方法を提供すること。
【解決手段】ギ酸の存在下で、オレフィンと過酸化水素とを反応させ、得られた反応混合物とアルコールとを反応させることを特徴とする１，２－アルカンジオールの製造法。
【選択図】なし

【特許請求の範囲】
【請求項１】
ギ酸の存在下で、オレフィンと過酸化水素とを反応させ、得られた反応混合物とアルコールとを反応させることを特徴とする１，２－アルカンジオールの製造法。
【請求項２】
オレフィンが、式：
$R^1R^2C=CR^3R^4$ （Ｉ）
（式中、R^1、R^2、R^3およびR^4は、それぞれ独立して、水素原子、置換基を有していてもよいアルキル基または置換基を有していてもよいアリール基を示すが、R^1、R^2、R^3およびR^4のうちの２つの基が一緒になって環を形成していてもよい）
で表されるオレフィンである請求項１記載の製造法。
【請求項３】
過酸化水素の量が、オレフィンの二重結合に対して、０．５～１当量である請求項１または２記載の製造法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、１，２－アルカンジオールの製造法に関する。さらに詳しくは、潤滑油、化粧品、香料、医薬品などの原料として有用な１，２－アルカンジオールの製造法に関する。
【背景技術】
【０００２】
１，２－アルカンジオールの製造法として、ギ酸または酢酸の存在下で、オレフィンと過酸化水素とを反応させ、生成したエポキシドを加水分解させる方法が知られている（例えば、非特許文献１および２参照）。しかし、この方法には、反応終了後に、溶媒の除去、水酸化ナトリウム水溶液との反応、および塩酸による中和などの多段階の操作を必要とするため、製造効率の点で欠点がある。
【０００３】
また、１，２－ジオールの製造法として、過酢酸を酸化剤として用い、オレフィンからエポキシドを経由して１，２－ジオールを製造する方法が知られている（例えば、特許文献１参照）。しかし、この方法には、エポキシドとジオールによる副生成物が生じるという欠点がある。
【０００４】
一方、エポキシドとジオールによる副生成物が生じることを回避しうる１，２－ジオールの製造法として、触媒としてタングステン錯体の存在下で、過酸化水素水とオレフィンとを反応させて１，２－ジオールを製造する方法が知られている（例えば、非特許文献３～５参照）。しかし、この方法には、生成したジオールがさらに酸化されるため、ケトンやカルボン酸を副生するという欠点がある。
【０００５】
反応条件を工夫することにより、１，２－ジオールの選択性を高める方法も提案されている（例えば、特許文献２および非特許文献６参照）。しかし、この方法には、毒性の高いベンゼンを溶媒として用いるため、作業環境における安全性に欠点があり、さらに生成物を単離するために３０％硫酸水溶液で抽出し、塩基で中和するという煩雑な操作を必要とするため、製造効率の点でも欠点がある。
【０００６】
また、他の１，２－ジオールの製造法として、濾過により容易に分離することができる固体触媒を用いてオレフィンと過酸化水素水とを反応させる方法が提案されている（例えば、非特許文献７～９参照）。しかし、この方法には、反応操作上での改善が認められるが、目的化合物とともにエポキシドやケトンを多量に生じるため、１，２－ジオールの収率および選択性が低いという欠点がある。

【０００７】
他の１，２－ジオール類の製造法として、スルホン酸基を有する高分子化合物の存在下に、オレフィン類と過酸化水素とを反応させることを特徴とする１，２－ジオール類の製造法が提案されている（例えば、特許文献３参照）。しかし、この方法には、反応時間をはじめ、効率面や安全性の面で欠点がある。
【０００８】
また、従来の１，２－アルカンジオールには、微量の不純物が含まれていることなどにより臭気が強いものが多いため、香料、化粧品などの用途に原料として用いられる１，２－アルカンジオールには、低臭気であることが求められている。
【０００９】
【特許文献１】特開平４－４１４４９号公報
【特許文献２】欧州特許第１４６３７４号明細書
【特許文献３】特開２００３－２１２８０４号公報
【非特許文献１】オーガニック・シンセシス(Organic Syntheses), Coll. ３巻、２１７－２１９頁（１９５５年）
【非特許文献２】ジャーナル・オブ・アメリカン・ケミカル・ソサイエティー(J. Am. Chem. Soc.）６７巻、１７８６－１７８８頁（１９４５年）
【非特許文献３】ジャーナル・オブ・ケミカル・ソサイエティー(J. Chem. Soc.)２９８８－３０００頁（１９４９年）
【非特許文献４】ジャーナル・オブ・アメリカン・オイル・ケミカル・ソサイエティー(J. Am. Oil Chem. Soc.）４４巻、３１６－３２０頁（１９６７年）
【非特許文献５】テトラヘドロン・レターズ(Tetrahedron Lett.）２９巻、８２３－８２６頁（１９８８年）
【非特許文献６】シンセシス(Synthesis）２９５－２９７頁(１９８９年)
【非特許文献７】ジャーナル・オブ・キャタリスト(J. Cat.）１４５巻、１５１－１５８頁（１９９４年）
【非特許文献８】ケミカル・コミュニケーションズ(Chem. Commun.）３２５－３２６頁(１９９８年)
【非特許文献９】ジャーナル・オブ・キャタリスト(J. Cat.）１８９巻、４０－５１頁（２０００年）
【発明の開示】
【発明が解決しようとする課題】
【００１０】
本発明は、前記従来技術に鑑みてなされたものであり、低臭気の１，２－アルカンジオールを高純度で容易かつ安全に製造しうる方法を提供することを課題とする。
【課題を解決するための手段】
【００１１】
本発明者らは、前記従来技術に鑑みて鋭意研究を重ねた結果、ギ酸の存在下で、オレフィンと過酸化水素とを反応させ、得られた反応混合物とアルコールとを反応させた場合には、１，２－アルカンジオールが高純度で容易に得られ、しかも得られた１，２－アルカンジオールは、臭気をほとんど生じさせないという驚くべき効果が奏されることを見出した。
【００１２】
本発明は、かかる知見に基づいて完成されたものであり、ギ酸の存在下で、オレフィンと過酸化水素とを反応させ、得られた反応混合物とアルコールとを反応させることを特徴とする１，２－アルカンジオールの製造法に関する。
【発明の効果】
【００１３】
本発明の製造法によれば、低臭気の１，２－アルカンジオールを高純度で容易かつ安全に製造することができるという効果が奏される。

【発明を実施するための最良の形態】

【００１４】

本発明においては、まず、ギ酸の存在下で、オレフィンと過酸化水素とを反応させる。

【００１５】

オレフィンとしては、種々のものを広範囲で用いることができる。代表的なオレフィンとしては、例えば、式（Ｉ）：

$$R^1R^2C=CR^3R^4 \qquad (I)$$

（式中、R^1、R^2、R^3およびR^4は、それぞれ独立して、水素原子、置換基を有していてもよいアルキル基または置換基を有していてもよいアリール基を示すが、R^1、R^2、R^3およびR^4のうちの２つの基が一緒になって環を形成していてもよい）

で表されるオレフィンが挙げられ、これらは、それぞれ単独でまたは２種以上を混合して用いることができる。

【００１６】

アルキル基としては、炭素数１～３５のアルキル基が好ましく、炭素数が１～２１のアルキル基がより好ましい。アルキル基が有していてもよい置換基としては、例えば、水酸基、炭素数１～２２のアルコキシ基などが挙げられる。

【００１７】

アリール基としては、炭素数６～３５のアリール基が好ましく、炭素数６～２２のアリール基がより好ましい。アリール基が有していてもよい置換基としては、例えば、水酸基、フェニル基、炭素数１～２２のアルコキシ基などが挙げられる。

【００１８】

なお、R^1、R^2、R^3およびR^4のうちの２つの基が一緒になって環を形成していてもよい。かかる環の例としては、炭素数３～３５のシクロアルキル基などが挙げられ、また、これらの環は他の環と縮合環、非縮合環等の多環を形成していてもよい。更にはR^1、R^2、R^3及びR^4の何れか１つから水素原子を取り除いた残基が２価の原子及び／又は２価の官能基を介して互いに結合して、それらが結合している炭素原子と一緒になって環を形成していてもよいが、この場合の２価の原子としては、酸素原子、窒素原子、硫黄原子等が、また２価の官能基としてはシリレン基、エチレンジオキシ基、アリーレンジオキシ基、カルボニル基、スルホキシド基、スルホン基等が例示される。

【００１９】

式（Ｉ）で表されるオレフィンの具体例としては、１－ヘキセン、２，３－ジメチル－２－ブテン、２－メチル－２－ペンテン、２－ヘプテン、シクロペンテン、シクロヘキセン、１－メチルシクロヘキセン、シクロオクテン、シクロドデセン、１－ウンデセン、１－ドデセン、２－シクロヘキセン－１－オール、１－エチル－１－シクロペンテン、けい皮アルコール、２－メチル－３－フェニル－２－プロペン－１－オール、４－（１－プロペニル）－１，２－ジメトキシベンゼンなどが挙げられる。

【００２０】

過酸化水素は、通常、水溶液として用いられる。過酸化水素水溶液における過酸化水素の濃度には特に制限がないが、通常、好ましくは１～８０％、より好ましくは３～６０％である。

【００２１】

過酸化水素の量は、オレフィンの二重結合に対して、当量以下が好ましい。通常、過酸化水素の量は、過酸化水素がオレフィンに対して過剰な場合は、反応後に過剰の過酸化物を処理する必要があり、場合によっては処理に用いたものの洗浄分離や濾過による除去工程も必要となる点、また過酸化物の処理剤により臭気成分が発生したり副反応物が生成したりする（通常、チオ硫酸ナトリウムなどの場合は、その硫黄原からの臭気が発生しやすく、酸化マンガンなどの触媒の場合には、ジオールの酸化などの副反応や、発熱による臭気成分や不純物が生じやすい）場合が多い点、および過酸化物過剰による危険性の増加による安全面の観点から、オレフィンの二重結合に対して、好ましくは０．５～１当量、より好ましくは０．７～０．９５当量である。

【００２２】
ギ酸の量は、オレフィンの酸化をより温和な条件で安全に進行させるため、反応系内において過ギ酸を生成させること、およびオレフィンから中間体として生成するエポキシ体とジオールとの副反応を抑制するため、エポキシ中間体をギ酸と反応させて開環させる観点から、通常、オレフィンの二重結合に対して、好ましくは１～３０当量、より好ましくは１～１５当量、生産効率の観点から、さらに好ましくは１～５当量である。
【００２３】
オレフィンと過酸化水素との反応は、例えば、オレフィンとギ酸とを混合した後、得られた混合物を撹拌しながら、該混合物に過酸化水素を添加する方法により、容易に行うことができる。
【００２４】
オレフィンと過酸化水素との反応温度は、通常、２０～１００℃、好ましくは３０～６０℃である。
【００２５】
なお、オレフィンと過酸化水素との反応の際には、溶媒を用いてもよい。溶媒としては、例えば、エーテル類、エステル類、ニトリル類、アミド類、スルホキシド類、炭化水素化合物などが挙げられる。溶媒の量は、特に制限されないが、一般的には、オレフィン１００容量部あたり、好ましくは１０００容量部以下、より好ましくは３００容量部以下である。
【００２６】
オレフィンと過酸化水素との反応の終点は、例えば、ガスクロマトグラフィーによる分析及び、過酸化物の滴定による過酸の消失確認などにより、容易に確認することができる。
【００２７】
かくしてオレフィンと過酸化水素との反応により、生成したエステルを含有する反応混合物が得られる。得られた反応混合物は、必要により、濃縮してもよい。
【００２８】
次に、得られた反応混合物とアルコールとを反応させる。かかる反応は、具体的には、得られた反応混合物に含まれている生成したエステルとアルコールとのエステル交換反応である。
【００２９】
アルコールとしては、例えば、炭素数１～４の直鎖または分岐鎖を有する１価アルコールが挙げられる。かかる１価アルコールの具体例としては、メタノール、エタノール、イソプロパノールなどが挙げられるが、本発明は、かかる例示のみに限定されるものではない。
【００３０】
アルコールの量は、反応混合物に含まれるエステル部位と残留しているギ酸を完全にギ酸エステル化する観点から、反応混合物に含まれている生成したエステルのエステル部と残留しているギ酸の合計に対して、好ましくは１～１０当量、より好ましくは２～１０当量、さらに好ましくは３～５当量である。
【００３１】
なお、得られた反応混合物とアルコールとの反応の際には、触媒を用いることができる。触媒としては、一般にエステル交換反応の際に使用されるものであればよい。触媒の例としては、硫酸、パラトルエンスルホン酸などのスルホニル化合物、スルホン酸基を有する高分子化合物などの酸触媒、リチウム化合物、チタン化合物、ナトリウム化合物、アルミニウム化合物、スズ化合物、亜鉛化合物などの金属触媒などが挙げられるが、本発明は、かかる例示のみに限定されるものではない。
【００３２】
触媒の量は、特に制限されないが、一般的には、反応混合物１００重量部あたり、好ましくは０．０１～５重量部、より好ましくは０．０５～１重量部である。

【００３３】
また、オレフィンと過酸化水素との反応は、通常溶媒を用いずに行うこともできるが、溶媒を用いることも可能である。溶媒としては、一般に酸化反応やエステル交換反応の際に使用されるものを用いることができる。溶媒の例としては、エーテル類、ニトリル類、アミド類、スルホキシド類、炭化水素化合物などが挙げられる。溶媒の量は、特に制限されないが、一般的には、オレフィン１００容量部あたり、好ましくは５０～１０００容量部、より好ましくは１００～３００容量部である。
【００３４】
得られた反応混合物とアルコールとの反応は、例えば、反応混合物に、アルコールおよび必要により触媒を添加し、混合することによって行うことができる。
【００３５】
反応温度は、通常、２０～８０℃の範囲内であることが好ましく、生成するギ酸エステルを選択的に反応系外へ出して、平衡反応を進行させる観点から、用いられるアルコールの沸点以下および生成するギ酸エステルの沸点以上であることがより好ましい。反応の際には、生成するギ酸エステルを回収することが好ましいが、特に、アルコールとしてメタノールを用いた場合には、他のギ酸エステルに比べて沸点が低いギ酸メチルが生成するため、より温和な条件下で反応混合物とアルコールとの反応を行うことができ、またメタノールとギ酸メチルは共沸せず、ギ酸メチルのみが揮発するため、ギ酸メチルを容易に反応系外に除去することができる。
【００３６】
反応混合物とアルコールとの反応は、通常溶媒を用いずに行うこともできるが、溶媒を用いることも可能である。溶媒としては、エステル交換反応の際に使用されるものを用いることができる。溶媒の例としては、エーテル類、ニトリル類、アミド類、スルホキシド類、炭化水素化合物などが挙げられる。
【００３７】
反応混合物とアルコールとの反応の終点は、例えば、ガスクロマトグラフィーによる分析などにより容易に確認することができる。
【００３８】
かくして、目的化合物である１，２－アルカンジオールが得られる。なお、反応の際に触媒を用いた場合には、生成した１，２－アルカンジオールを含有する反応混合物にアルカリを添加することにより、触媒を中和することが好ましい。
【００３９】
なお、１，２－アルカンジオールを含有する反応混合物に含まれているギ酸エステル、ギ酸およびアルコールは、反応混合物を濃縮することにより回収し、再利用することができる。得られた１，２－アルカンジオールは、例えば、蒸留などによって精製してもよい。また、１，２－アルカンジオールが、水と混合した際に少なくとも水層への移行が可能な程度の水溶性を示す場合には、１，２－アルカンジオールを、ノルマルヘキサン、シクロヘキサン、２－メチルヘキサン等の疎水性溶剤及び水と混合することにより、臭気成分は有機層に、１，２－アルカンジオールは水層にそれぞれ移行し、より臭気の低減された１，２－アルカンジオールを水層に抽出することができる。
【００４０】
本発明の製造法は、毒性の高いベンゼンなどの溶媒を必要しないので、作業環境における安全性に優れている。また、本発明の製造法によれば、１，２－アルカンジオールを高純度でかつ高収率で容易に得ることができる。さらに、本発明の製造方法で得られた１，２－アルカンジオールは、ほとんど臭気を発しないので、潤滑油、化粧品、香料、医薬品などの原料として好適に使用することができる。
【実施例】
【００４１】
次に、本発明を実施例に基づいてさらに詳細に説明するが、本発明はかかる実施例のみに限定されるものではない。

【００４２】
実施例１
（１）オレフィンと過酸化水素との反応
１－ヘキセン１００ｇおよびギ酸（純度９５％）２３７．５ｇを１リットル容のビーカー内で混合し、得られた混合物を攪拌しながら加熱し、３０℃に到達した時点で３５％過酸化水素水溶液９８．２ｇを１０時間かけてゆっくりと前記混合物に添加した。反応により発熱するので、混合物の温度が３０～４０℃となるように外部から冷却した。
【００４３】
過酸化水素水溶液の添加終了後、混合物の温度を３５℃で２時間保持することにより、反応を終了した。反応の終点は、過酸化物量の滴定(ヨウ化カリウム滴定法)により確認した。得られた反応混合物を過剰分のギ酸の留出が少なくなるまで(ギ酸もギ酸エステルとなるため完全に濃縮する必要は無い)となるまで濃縮し、濃縮された反応混合物を次のアルコールとの反応に供した。
【００４４】
（２）反応混合物とアルコールとの反応
前記（１）で得られた濃縮された反応混合物１７６．７ｇ、メタノール１７０ｇおよびパラトルエンスルホン酸一水和物０．０９ｇを１リットル容のビーカー内で混合し、生成するギ酸メチルをビーカーから取り出しながら５５℃で７時間攪拌した。その後、ビーカー内に３０％水酸化ナトリウム水溶液０．０８ｇを添加し、触媒（パラトルエンスルホン酸一水和物）の中和を行った後、メタノールを減圧下で留去し、１，２－ヘキサンジオール１２０．７ｇを得た。その結果、１，２－ヘキサンジオールの収率は９２％であり、１，２－ヘキサンジオールの純度は、９２％であった。
【００４５】
次に、得られた１，２－ヘキサンジオールを蒸留により精製したところ、収率７６％、初留をさらに再蒸留することにより、蒸留収率９４％で、９８％以上の純度を有する１，２－ヘキサンジオールが得られた。
【００４６】
実施例２
実施例１と同様にして１，２－ヘキサンジオールを製造し、蒸留による精製まで行った。得られた１，２－ヘキサンジオール５ｇ（純度９８％）、ノルマルヘキサン１０ｇおよび水１０ｇを２５℃で混合撹拌した。ヘキサン層を分離し、水層を濃縮し、臭気成分が除去された、１，２－ヘキサンジオール４．９ｇ（ノルマルヘキサンおよび水と混合した１，２－ヘキサンジオールに対する収率９８％、純度９９％）を得た。
【００４７】
実施例３～９
１－ヘキセンの代わりに表１に示すオレフィンを使用し、ギ酸、過酸化水素水溶液等を表１に示す量で使用した以外は、実施例１と同様にして、１，２－アルカンジオールを得た。得られた１，２－アルカンジオール及びその収率、純度を表１に示す。
【００４８】

7/31/2019, EAST Version: 4.1.2.6

【表１】

	（１）					（２）			得られた1,2-アルカンジオール			
	オレフィン		ギ酸 (g)	35%過酸化水素水溶液 (g)	過酸化水素水溶液の添加時間 (hr)	反応混合物 (g)	メタノール (g)	パラトルエンスルホン酸一水和物 (g)	種類	収量 (g)	収率 (%)	純度 (%)
	種類	使用量 (g)										
実施例1	1-ヘキセン	100.0	237.5 (4.1)	98.2 (0.85)	10	176.7	170	0.09	1,2-ヘキサンジオール	120.7	92	92
実施例3	4-メチル-1-ペンテン	100.0	259.1 (4.5)	98.2 (0.85)	10	170.7	170	0.09	4-メチル-1,2-ペンタンジオール	121.9	91.9	90
実施例4	シクロヘキセン	10.0	26.5 (4.5)	10.1 (0.85)	10	175.0	17	0.009	1,2-シクロヘキサンジオール	12.0	93.9	94
実施例5	1-ドデセン	10.0	13.0 (4.5)	4.9 (0.85)	10	132.5	9	0.009	1,2-ドデカンジオール	10.2	88.8	89
実施例6	1-オクテン	15.1	29.2 (4.5)	11.1 (0.85)	12	20.1	29	0.1	1,2-オクタンジオール	15.1	90.7	99.1
実施例7	4,4-ジメチル-1-ペンテン	5.1	12.6 (5.0)	4.3 (0.85)	10	6.6	13	0.01	4,4-ジメチル-1,2-ペンタンジオール	4.7	82.6	99.5
実施例8	4-メチル-1-ヘキセン	7.0	17.2 (5.0)	5.9 (0.85)	10	9.2	18	0.02	4-メチル-1,2-ヘキサンジオール	6.0	75.6	98.7
実施例9	5-メチル-1-ヘキセン	6.6	42.6 (13.1)	5.6 (0.85)	10	9.6	9	0.02	5-メチル-1,2-ヘキサンジオール	6.2	97.5	99.6

注）ギ酸及び過酸化水素水溶液の使用量に記載の"()"内の数値は、ギ酸又は過酸化水素のオレフィンの二重結合に対する当量数を示す。

【００４９】

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比較例１

シクロヘキセン４１ｇをガラスのフラスコに仕込み、攪拌しながら３０℃に昇温する。３０℃に達したところで３０％の過酢酸をモル比で１．２倍になるように２時間かけてゆっくり添加した。反応により発熱するので混合物の温度が３０℃程度になるように、外部から冷却した。過酢酸の添加終了後、混合物の温度を３０℃で１時間保持することにより、反応を完結させた。反応粗液を、ガスクロマトグラフィーにより分析した結果、シクロヘキセンオキシドが収率の９３％で得られていることを確認した。

【００５０】

水５０ｇをガラス製のフラスコに仕込み、撹拌しながら加熱し、７０℃に到達した時点で、前記で得られたシクロヘキセンオキシドおよび酢酸を含む溶液２１．６ｇを２時間かけてゆっくり添加した。溶液の添加終了後、すぐに反応粗液をガスクロマトグラフィーにより分析した結果、シクロヘキサン－１，２－ジオールが、シクロヘキセンオキシド基準では９４％の収率で、シクロヘキセン基準では８７．４％の収率で得られていることを確認した。

【００５１】

比較例２

Ｎａｆｉｏｎ－ＮＲ５０（ＤｕＰｏｎｔ社製）５００ｍｇ(オレフィンに対するスルホン酸基の当量は０．０４に相当）、３０％過酸化水素水溶液２．２３ｇ（１９．６ｍｍｏｌ）および１－ヘキセン８２５ｍｇ（９．８１ｍｍｏｌ）を混合し、７０℃で２４時間撹拌した。ガスクロマトグラフィーで反応溶液を分析した結果、ほとんど反応の進行は認められなかった。

【００５２】

反応溶液からＮａｆｉｏｎ－ＮＲ５０を濾過して取り除き、溶液中に過剰に存在する過酸化水素を分解するため二酸化マンガン１０ｍｇ（０．１１５ｍｍｏｌ）を加えた。反応溶液を濾過した後、ロータリーエバポレーターを用いて水等を留去したところ、１，２－ヘキサンジオールを濃縮混合物として得た（収率：５％未満）。

【００５３】

比較例３

実施例１の（１）オレフィンと過酸化水素との反応と同様にして得られた、濃縮された反応混合物１７６．７ｇに、３０％水酸化ナトリウム水溶液２３９．３ｇを、２０～３５℃で滴下した。反応の終点は、ガスクロマトグラフィーによる分析により確認した。得られた反応混合物に、抽出溶剤のメチルターシャリーブチルエーテル１４２．４ｇを加え、撹拌後、静置しギ酸カリウムが含まれる水層を分離した。有機層に、２０％食塩水７１．２ｇを加え洗浄し、撹拌、静置後水層を分離した。この洗浄操作を合計３回行った後、有機層を濃縮しメチルターシャリーブチルエーテルを取り除き、１，２－ヘキサンジオール１１８．１ｇを得た。その結果、１，２－ヘキサンジオールの収率は８５．２％であり、１，２－ヘキサンジオールの純度は８５％であった。また、この１，２－ヘキサンジオールには、溶剤由来の臭気や、強アルカリ処理による着臭がみられた。

【００５４】

実験例

実施例１～９および比較例１、３で得られた１，２－アルカンジオールと、これらを精製水で２０倍に希釈した５重量％１，２－アルカンジオール水溶液を用意した。

【００５５】

１００ｍＬ容のガラス製広口瓶に、前記で用意した１，２－アルカンジオールまたは５重量％１，２－アルカンジオール水溶液を入れ、無作為に抽出した男女２０名の各パネラーに、瓶口での臭気を確認してもらい、１，２－アルカンジオールおよび５重量％１，２－アルカンジオール水溶液のそれぞれについて、以下の評価基準に基づいて評価してもらった。結果を表２に示す。なお、実施例および比較例で得られた１，２－アルカンジオール自体は、無臭の化合物である。

【００５６】

〔評価基準〕
○：ほぼ無臭である。
△：わずかに臭う。
×：臭気が明らかに感じられる。
【００５７】
次に、上記の結果に基づいて、各評価を行った者の人数を集計し、以下の基準にしたがってランク付けを行なった。なお、Ｓ以上のランクが合格である。
【００５８】
〔ランク〕
ＳＳＳ：○の評価をした評価者が１８名以上である場合
ＳＳ：○の評価をした評価者が１５～１７名であり、×の評価をした評価者がひとりもいない場合
Ｓ：○の評価をした評価者が１５～１７名であり、×の評価をした評価者がいる場合
Ａ：○の評価をした評価者が１０～１４名である場合
Ｂ：○の評価をした評価者が５～９名である場合
Ｃ：○の評価をした評価者が４名以下である場合
【００５９】
【表２】

実施例番号	臭気の有無	
	1,2-アルカンジオール	5重量%1,2-アルカンジオール水溶液
1	ＳＳ	Ｓ
2	ＳＳＳ	ＳＳ
3	ＳＳ	Ｓ
4	ＳＳ	Ｓ
5	Ｓ	Ａ
6	Ｓ	Ａ
7	ＳＳ	Ｓ
8	ＳＳ	Ｓ
9	ＳＳ	Ｓ
比較例1	Ａ	Ｂ
3	Ｂ	Ｃ

【００６０】
表１に示された結果より、実施例１～９の方法によれば、生成した１，２－アルカンジオールの臭気が比較的生じがたい従来の比較例１、３と対比しても、著しく１，２－ヘキサンジオールの臭気を低減させることができることがわかる。
【００６１】
また、実施例１～９によれば、毒性の高いベンゼンなどの溶媒を必要しないので、作業

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環境における安全性に優れており、しかも従来、必要とされていた過酸化物のチオ硫酸ナトリウムやマンガン触媒をはじめとした過酸処理や、エステルの強アルカリによる処理などの操作を必要とせず、また酸化反応を従来よりも低い温度で行うことができるため、臭気が低減された１，２－アルカンジオールを容易にかつ効率よく安全に製造することができることがわかる。

【００６２】

したがって、本発明の製造法によれば、潤滑油、化粧品、香料、医薬品などの原料として有用な１，２－アルカンジオールを高純度で容易かつ安全に製造することができることがわかる。

【産業上の利用可能性】

【００６３】

本発明の製造法によって得られた１，２－アルカンジオールは、潤滑油、化粧品、香料、医薬品などの原料として好適に使用することができる。

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Method for synthesizing 1,2-pentanediol by one-pot method

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Abstract of CN104926600 (A)

The invention relates to a method for high-yield synthesis of 1,2-pentanediol from n-pentene under low-temperature condition by a one-pot method. According to the method, the reaction temperature is low, so that the risk of leakage caused by high-temperature volatilization of a 1-pentene raw material, and meanwhile, the requirements on pressure resistance of equipment are lowered; by adopting a multistep one-pot method process, process flows are shortened; corrosive, polluting and harmful compounds are not adopted as raw materials during reaction, so that the condition in the traditional process that an organic acid oxygen carrying agent, of which the weight is multiple that of the raw materials, is adopted is avoided; the environment-friendliness of the process is good; and the method has the advantages that the source of raw materials is wide, the production cost is low, and the economical efficiency is high.

DESCRIPTION CN104926600

The invention relates to a method for synthesizing 1,2-pentanediol by high-yield one-pot method from n-pentene as a raw material under low temperature conditions. The reaction temperature of the invention is low, the high temperature volatilization of the 1-pentene raw material is lowered to cause leakage risk, and the pressure resistance requirement of the device is reduced; the multi-step one-pot process is used to shorten the process flow; the reaction is not corroded, The pollution and harmful compounds are used as raw materials, and the organic acid oxygen carrier is used in the traditional process. The process is environmentally friendly; the raw materials of the invention have wide sources, low production cost and good economy.

Method for synthesizing 1,2-pentanediol by one-pot method

Technical field

The invention relates to a one-pot method for synthesizing 1,2-pentanediol, belonging to the field of organic compound synthesis.

Background technique

1

,2

-Pentanediol is an important intermediate for the synthesis of propiconazole fungicides with high activity, low toxicity and broad spectrum of activity (developed by Belgian Janssen Pharmaceutical Group < 1 >, registered in many countries) for the construction of propiconazole molecules. The ketal structure < 2 > . 1,2-Pentanediol also has a moisturizing function, and it is synergistic with other humectants to produce a strong synergistic effect <3>, which can be used as a moisturizing ingredient in cosmetics or personal care products < 3-4 >. 1,2-Pentanediol also has a bacteriostatic < 5 > and can effectively inhibit product deterioration < 6 > in formulations without the addition of other preservatives.

1,2 - The synthesis method of pentanediol is mainly the following two types: (1) epoxidation of n-pentene and subsequent hydrolysis; (2) hydrogenation reduction of furfural or decyl alcohol. The first method mainly has the disadvantages of production safety and pollution. The second method mainly has shortcomings such as low conversion rate of raw materials, many side reactions and difficulty in product purification. The specific conditions are as follows.

Degussa < 7 > discloses a method for synthesizing 1,2-pentanediol from a continuous phase of n-pentene as a raw material, benzene as a solvent, propionic acid as an oxygen-carrying agent and sodium hydroxide as a ring-opening reagent. Ciba-Geigy discloses a continuous production process for the synthesis of 1,2-pentanediol using n-pentene and formic acid as raw materials, hydrogen peroxide as the oxidant and sodium hydroxide as the ring-opening reagent. Zhejiang Liansheng Group < 9 > and Sinopec < 10 > also disclosed similar processes using n-pentene, formic acid and hydrogen peroxide as raw materials. The raw material of the process has a low boiling point (the boiling point of n-pentene is 30.1 ° C), which is easy to cause labor safety and production safety due to volatilization of low-boiling organic compounds; the corrosion of the equipment is strong with formic acid as a raw material, and a small amount of leaked formic acid is used. The operator's skin has a strong corrosive effect, and a large amount of liquid organic waste is treated with 2-10 times of formic acid in the amount of n-pentene material; the by-product of the reaction is many, and the separation and purification of the product is relatively difficult. Dalian Institute of Chemical Industry < 11 > discloses a method for directly preparing 1,2-fatty diol by reacting n-pentene with hydrogen peroxide by phosphotungstic acid, and solves a series of problems caused by excessive formic acid; Under the reaction conditions, low-boiling raw materials volatilize and high pressure resistance requirements for equipment are insufficient. Zhu Yulei, Institute of Coal, Chinese Academy of Sciences < 12 > reported a new green chemical route for the synthesis of 1,2-pentanediol. The manganese dioxide-loaded noble metal ruthenium catalyzed hydrogenation of decyl alcohol to 1,2-pentanediol. The noble metal ruthenium is used in the method, which is expensive; and the supported carrier manganese dioxide is not a carrier material which is particularly suitable for industrial applications. Hou Wei of Tianjin Medical University < 13 > reported that n-pentene is used as raw material, sodium borate is used as oxidant, acetic anhydride is used as reaction solvent and reactant to synthesize monopentyl acetate. The ester compound is further hydrolyzed under alkaline conditions. 1,2-pentanediol. This method avoids highly corrosive compounds such as formic acid. However, excessive acetic anhydride and oxidant lead to difficult post-treatment of the reaction product; stoichiometric reaction of n-pentene with acetic anhydride produces monopentyl acetate, which consumes a large amount of acetic anhydride, increases the cost of raw materials; oxidation reaction forms monoester and hydrolysis The separation of the reaction prolongs the reaction route and increases the operating cost. Severeyns et al. < 14 > catalyze the bis-hydroxylation of n-pentene to synthesize a 1,2-pentanediol diol by the action of NMO and osmium tetroxide catalyst. The ruthenium osmium catalyst used in the method has high toxicity, high price, and is apt to generate toxic gas by heat, so the industrial application value of the route is extremely small.

As early as 1931, Adkins < 15 > reported that copper chromite catalyzed the hydrogenation of sterol to synthesize a mixture of 1,2-pentanediol and 1,5-pentanediol, and added 0.7 g of sterol to 3 g of catalyst at 175 < o > The reaction under C for 11 hours, the total yield of 1,2-pentanediol and 1,5-pentanediol was up to 70%. However, in 1958, Manly used a similar reaction condition of Adkins, and the yield of 1,2-pentanediol was only 4.4%. Tomishige < 17 > at the University of Tsukuba, Japan, published a metal-supported ruthenium and rhodium-catalyzed hydrogenation reduction of decyl alcohol at Chem Comm. As a result, no 1,2-pentanediol was detected in the product, but a selective generation of 1 , 5-pentanediol. Xu Yanjuan of Zhejiang University < 18 > studied Cu-Zn, Cu-Mn, Cu-Cr, Raney Cu, Raney Ni and noble metal supported catalysts Pt/C, Pd/C, Ru/ Al2O3 and other catalytic decyl alcohol selective hydrogenation reduction 1,2-pentanediol, wherein Cu-Zn has the best catalytic performance. The reaction temperature was 150~160 < o > C, the reaction pressure was 7~8MPa, the reaction time was 10h, the conversion of sterol reached 69.2%, the selectivity of 1,2-pentanediol reached 46.2%, and the yield reached 32.0. %. Low conversion of raw materials, high side reactions and low yields of 1,2-pentanediol are still fatal defects in this route. Evonik Industries Group < 19 > discloses a method for the hydrogenation reduction of decyl alcohol to 1,2-pentanediol. Zhuhai Kaimei Technology Co., Ltd. < 20 > discloses the selective hydrogenation of non-precious metal catalysts to 1,2-pentanediol. The method utilizes the deep processing product furfural as raw material of agricultural and sideline products, and greatly solves the problem of limitation of raw materials by n-pentene; the method uses catalytic hydrogenation of non-precious metal catalysts such as copper oxide to solve the problems of expensive and difficult recovery of precious metal catalyst; The method still has problems such as incomplete conversion of raw materials, many side reactions and low yield, which brings new problems such as difficulty in separation, low product purity and non-environmental friendly reaction route; poor performance of catalytic hydrogenation of copper oxide leads to poor performance. The pressure of the hydrogenation reaction is too high, which leads to safety hazards in the production process. Maya Chatterjee < 21 > from the Sendai Chemical Research Center in Sendai, Japan, reported the synthesis of 1,2-pentanediol from tetrahydrofurfuryl alcohol in supercritical carbon dioxide, in which Pd/MCM-41 is the catalyst for 1,2-pentanediol. The highest rate, reaching 77.4%, also contained 12.6% of 1,5-pentanediol and 10% of a mixture of 1-pentanol and 2-pentanol. Although the method improves the yield of 1,2-pentanediol, the supported noble metal is still used as a catalyst, and the operation cost is relatively high; using supercritical carbon dioxide as a solvent, the pressure of the reaction system is also large, and the process is not Suitable for the production of 1,2-pentanediol on an industrial scale.

In addition to the above two methods, there are some sporadic reports on the synthesis of 1,2-pentanediol. Degussa Company < 22 > discloses the nucleophilic reaction of n-butyraldehyde with hydrocyanic acid to form o-hydroxyl-valeronitrile, hydrolyzing o-hydroxy-n-valeronitrile to obtain o-hydroxy-n-pentanol, and then catalyzing a heterogeneous catalyst such as noble metal ruthenium and osmium. Synthesis of 1,2-pentanediol. In the method, the raw material hydrocyanic acid is a highly toxic chemical, which is potentially fatal to the operator; the reaction is carried out in three steps, and the route is long; the first step of the nucleophilic reaction is difficult to control the reaction due to side reactions such as aldol condensation, by-products More, product purification is difficult; the use of precious metals lanthanum and cerium as a catalyst increases production costs. Jiangsu Yangnong Chemical Group < 23 > discloses the epoxidation of 2-chloropentanol in an alkaline solvent. Although the process may obtain 1,2-pentanediol in a high yield, the raw material of 2-chloropentanol is not easily obtained, and the atmospheric distillation of the pentylene oxide in the reaction process has a fatal hidden danger of unsafe operation. Ding Xiaobing of Jiangsu Chemical Pesticide Group reported in "Anhui Chemical" < 24 > Reduction of 1,2-pentanediol by o-hydroxy-n-valeric acid with sodium borohydride. The high cost of sodium borohydride and the inability to obtain hydroxy-p-pentanoic acid make the process difficult to achieve industrial production.

In summary, it has been reported in the literature that the route of synthesizing 1,2 pentanediol by cyclopentene epoxidation reaction and epoxy compound ring-opening reaction has low boiling point and high volatility of raw materials, and liquid waste generated by the process. Many, product separation and post-processing difficulties are not enough; it has been reported in the literature that the route of synthesizing 1,2-pentanediol by hydrogenation reduction of decyl alcohol or furfural solves the problem of raw material source, but the precious metal catalyst still exists. Insufficient conversion rate of raw materials, poor product selectivity and low product purity; other methods reported may have high raw material prices, insufficient source of raw materials, or use of highly toxic chemicals in the reaction process, or long route or reaction Difficulties, or difficulty in product purification.

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Summary of the invention

[Questions to be solved]

It is an object of the present invention to provide a process for synthesizing 1,2-pentanediol from n-pentene as a raw material under low temperature conditions.

Another object of the present invention is to provide a process for synthesizing 1,2-pentanediol from a raw material which is non-corrosive to equipment.

Another object of the present invention is to provide a more environmentally friendly process for the synthesis of 1,2-pentanediol from 1-pentene.

[Technical solutions]

The method of the present invention comprises the following steps:

1 Adding a certain amount of solvent and catalyst to the reaction kettle and mixing them uniformly;

2 Adding a certain amount of n-pentene to the reaction vessel and mixing uniformly;

3 Keep the temperature of the material in the reactor at 0-40 < o > C, and slowly add a certain amount of hydrogen peroxide under slow stirring conditions for several hours;

4 Adding a certain amount of water or no water to the reaction kettle;

5 Adding a certain amount of manganese dioxide to the reaction kettle;

6 The temperature in the reactor is raised to 30-80 < o > C, and the reaction is for several hours;

7 After the reaction is completed, the solvent in the system is evaporated, and filtered to obtain a crude product of 1,2-pentanediol;

8 The above crude product was distilled under reduced pressure to obtain 1,2-pentanediol having a content of more than 99.5%.

[Beneficial effect]

Compared with the conventional synthesis method of 1,2-pentanediol, the beneficial effects of the present invention are as follows:

1 The reaction temperature provided by the invention is low heat, which reduces the high temperature volatilization of the 1-pentene raw material, leads to the risk of leakage and reduces the pressure resistance requirement for the equipment.

2 The multi-step one-pot reaction process provided by the invention has short route, simple processing and high product yield, and synthesizes 1,2-pentanediol.

3 The process of the invention has no corrosion, no pollution and no harmful compounds, so the synthesis process of the invention has better environmental friendliness.

4 The raw material of the method of the invention has wide source and low cost, short process route, low production cost and good economy.

DRAWINGS

Figure 1 is a Fourier transform infrared spectrum of a potassium bromide salt sheet coating method for 1,2-pentanediol. In the figure, 3361cm < -1 > is the stretching vibration absorption of the associated hydroxyl group; 2958 cm < -1 > , 2931 cm < -1 > and 2872 cm < -1 > are the hydrocarbon stretching vibrations of methyl and methylene groups. Characteristics of absorption.

2 is a gas chromatogram of the product 1,2-pentanediol of Example 2. The gas chromatographic conditions were: OV1701 capillary column, 30 m, 0.32 um, nitrogen as carrier gas, pre-column pressure 0.1 MPa, column temperature 180 < o > C. The area normalized percentage was 99.89%, and the content determined by the internal standard standard curve method using propylene glycol as the internal standard was 99.85%.

Detailed ways

The invention is further illustrated by the following examples, but the invention is not limited to the following examples.

Example 1

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of methanol and 0.1 g of titanium tetrachloride, mix slowly by slow stirring; under slow stirring conditions 10 g of n-pentene was added dropwise with a constant pressure dropping funnel; under 10 < o > C conditions, 15 g of 30% aqueous hydrogen peroxide solution was slowly added dropwise through a constant pressure separatory funnel at about 30 min, after the addition was completed. Stirring was continued for 6 h at 10 < o > C; then 20 g of water was added to the reactor and reacted for 5 h at 50 < o > C; 0.1 g of manganese dioxide was added to the reactor, and the solvent methanol was distilled off. The water was removed, and 10.3 g of a crude product of 1,2 pentanediol having a purity of 97.3% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered.

Example 2

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of methanol and 0.1 g of tetramethyl titanate respectively, mix slowly by slow stirring; in slow stirring conditions 10 g of n-pentene was added dropwise with a constant pressure dropping funnel; and under a condition of 10 < o > C, 14 g of a 50% aqueous solution of hydrogen peroxide was slowly added dropwise through a constant pressure separatory funnel at about 30 min. After the addition is completed, stirring is continued for 6 h at 10 < o > C; then 30 g of water is added to the reactor, and then reacted at 50 < o > C for 8 h; 0.1 g of manganese dioxide is added to the reactor, and distillation is carried out. The solvent methanol was recovered and the water was removed, and 13.0 g of a crude product of 1,2 pentanediol having a purity of 97.4% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered, and distilled under reduced pressure. A fraction of about 80 < o > C at 5 mmHg was collected to obtain 12.1 g of a 1,2-pentanediol product having a purity of 99.6% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard).

Example 3

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of isopropanol and 1.0 g of tetrabutyl titanate, mix slowly by slow stirring; Under the condition, 10 g of n-pentene was added dropwise by a constant pressure dropping funnel; 40 g of a 10% aqueous solution of hydrogen peroxide was slowly added dropwise to the constant pressure separatory funnel at 10 < o > C for about 30 min. After the addition was completed, stirring was continued for 10 h at 10 < o > C; the temperature of the system was raised to 80 < o > C, and the reaction was continued for 8 h; 0.1 g of manganese dioxide was added to the reactor, and the solvent was distilled to recover isopropanol. The water was removed, and 12.4 g of a crude product of 1,2 pentanediol having a purity of 95.2% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered.

Example 4

Add 20 mL of isopropanol and 2.0 g of tetraisopropyl titanate to an atmospheric reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux, and mix slowly with slow agitation; 10 g of n-pentene was added dropwise with a constant pressure dropping funnel under stirring; 20 g of a 20% aqueous solution of hydrogen peroxide was slowly added dropwise at 30 ° via a constant pressure separatory funnel at about 10 min. After the addition, the mixture was stirred at 10 < o > C for 10 h; then 20 g of water was added to the reactor, and then reacted at 60 < o > C for 5 h; 0.1 g of manganese dioxide was added to the reactor. The solvent was distilled to recover isopropanol and the water was removed, and filtered to obtain 13.2 g of a crude 1,2 pentanediol having a purity of 96.5% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard).

Example 5

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of ethanol and 1.5 g of tetrahexyl titanate, mix slowly by slow stirring; in slow stirring conditions 10 g of n-pentene was added dropwise with a constant pressure dropping funnel; 8 g of an aqueous solution of 80% hydrogen peroxide was slowly added dropwise at a pressure of 10 <0>C through a constant pressure separatory funnel at about 30 min. After the addition is completed, stirring is continued for 2 h at 40 < o > C; then 20 g of water is added to the reactor, and then reacted at 70 < o > C for 4 h; 0.1 g of manganese dioxide is added to the reactor, and distillation is carried out. The solvent ethanol was recovered and the water was removed, and 12.5 g of a crude product of 1,2 pentanediol having a purity of 95.3% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered, and distilled under reduced pressure. A fraction of about 80 < o > C at

5 mmHg was collected to obtain 11.2 g of a 1,2-pentanediol product having a purity of 99.5% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard).

Example 6

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 30 mL of acetone and 1.0 g of tetraisobutyl titanate respectively, mix slowly by slow stirring; in slow stirring conditions 10 g of n-pentene was added dropwise with a constant pressure dropping funnel; 20 g of a 30% aqueous solution of hydrogen peroxide was slowly added dropwise at a pressure of 10 <0>C through a constant pressure separatory funnel at 30 min. After the addition is completed, stirring is continued for 4 h at 20 < o > C; then 10 g of water is added to the reactor, and then reacted at 40 < o > C for 20 h; 0.1 g of manganese dioxide is added to the reactor, and distillation is carried out. The solvent acetone was recovered and the water was removed, and 12.7 g of a crude 1,2 pentanediol having a purity of 95.9% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered.

Example 7

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of methyl ethyl ketone and 0.3 g of titanium tetrachloride, mix slowly by slow stirring; under slow stirring conditions 10 g of n-pentene was added dropwise by a constant pressure dropping funnel; 12 g of a 30% aqueous solution of hydrogen peroxide was slowly added dropwise at a pressure of 10 <0>C through a constant pressure separatory funnel at 30 min. After completion, stir at 30 < o > C for 2 h; then add 10 g of water to the reactor, and then react at 50 < o > C for 16 h; add 0.1 g of manganese dioxide to the reactor, and recycle it. The solvent was subjected to methyl ethyl ketone and water was removed, and 11.2 g of a crude product of 1,2 pentanediol having a purity of 98.1% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered.

Example 8

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of tetrahydrofuran and 0.2 g of tetramethyl titanate respectively, mix slowly by slow stirring; under slow stirring conditions 10 g of n-pentene was added dropwise with a constant pressure dropping funnel; under a condition of 10 < o > C, 15 g of a 30% aqueous solution of hydrogen peroxide was slowly added dropwise through a constant pressure separatory funnel at about 30 min. After the addition is completed, stirring is continued for 1 h at 40 < o > C; then 20 g of water is added to the reactor, and then reacted at 50 < o > C for 4 h; 0.1 g of manganese dioxide is added to the reactor, and distillation is carried out. The solvent tetrahydrofuran was recovered and the water was removed, and 14.5 g of crude 1,2 pentanediol having a purity of 98.3% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered, and distilled under reduced pressure. A fraction of about 80 < o > C at 5 mmHg was collected to obtain 13.5 g of a 1,2-pentanediol product having a purity of 99.9% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard).

Example 9

In a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux device, add 20 mL of diethyl ketone and 0.3 g of tetraethyl titanate respectively, mix slowly by slow stirring; 10 g of n-pentene was added dropwise with a constant pressure dropping funnel under stirring; 10 g of a 50% aqueous solution of hydrogen peroxide was slowly added dropwise to the constant pressure separatory funnel at 10 < o > C for about 30 min. After the addition, the mixture was stirred at 20 < o > C for 10 h; then 20 g of water was added to the reactor, and then reacted at 50 < o > C for 4 h; 0.1 g of manganese dioxide was added to the reactor. Distilling solvent tetrahydrofuran and removing water, and filtering 13.7 g of crude 1,2 pentanediol having a purity of 98.0%

(gas chromatography, internal standard curve method of 1,2-propanediol internal standard); Distillation, collecting fractions of about 80 < o > C at 5 mmHg, yielding 12.4 g of 1,2-pentanediol with a purity of 99.7% (gas chromatography, internal standard curve method for 1,2-propanediol internal standard) product.

Example 10

Add 200 mL of anhydrous methanol and 3.0 g of tetramethyl titanate to a normal pressure reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux, and mix slowly by slow stirring; 200 g of n-pentene was added dropwise with a constant pressure dropping funnel under stirring; 300 g of a 30% aqueous solution of hydrogen peroxide was slowly added dropwise to the constant pressure separatory funnel at 10 < o > C for about 30 min. After the addition, the mixture was stirred at 10 < o > C for 10 h; then 200 g of water was added to the reactor, and then reacted at 50 < o > C for 14 h; 1 g of manganese dioxide was added to the reactor. Distilling solvent methanol and removing water, and filtering to obtain 290.2 g of a crude product of 1,2 pentanediol having a purity of 98.1% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard); Distillation, collecting fractions of about 80 < o > C at 5 mmHg, yielding 281.0 g of 1,2-pentanediol with a purity of 99.7% (gas chromatography, internal standard curve method for 1,2-propanediol internal standard) product.

Example 11

Add 200 mL of tetrahydrofuran and 3.0 g of tetramethyl titanate to an atmospheric reactor with heating, temperature control, magnetic stirring, constant pressure dropping and reflux, and mix slowly by slow stirring; 200 g of n-pentene was added dropwise with a constant pressure dropping funnel; 150 g of a 50% aqueous solution of hydrogen peroxide was slowly added dropwise at a pressure of 10 <0>C through a constant pressure separatory funnel at 30 min. After the addition is completed, the reaction is further stirred at 20 < o > C for 10 h; then 400 g of water is added to the reactor, and then reacted at 50 < o > C for 15 h; 1 g of manganese dioxide is added to the reactor. The solvent methanol was distilled off and the water was removed, and 292.0 g of a crude 1,2-pentanediol having a purity of 98.0% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was obtained by filtration; Collecting a fraction of about 80 < o > C at 5 mmHg to obtain 278.8 g of a 1,2-pentanediol product having a purity of 99.7% (gas chromatography, internal standard curve method for 1,2-propanediol internal standard) .

Example 12

200 mL of methanol, 3.0 g of tetramethyl titanate and 200 g of n-pentene were added to the autoclave with heating, temperature control and mechanical stirring; after mixing, 300 g of hydrogen peroxide at a concentration of 30% was added. The aqueous solution is then stirred at 60 < o > C for 2 h; 400 g of water is added, and then reacted at 60 < o > C for 10 h; the mixture is transferred to an atmospheric distillation unit, and the solvent methanol is distilled off. The water was removed, and 150.2 g of a crude 1,2 pentanediol having a purity of 64.0% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered.

Example 13

200 mL of tetrahydrofuran, 3.0 g of tetramethyl titanate and 200 g of n-pentene were added to the autoclave with heating, temperature control and mechanical stirring; after mixing, 150 g of 50% hydrogen peroxide was added. The aqueous solution is then stirred at 80 < o > C for 2 h; 400 g of water is added, and then reacted at 80 < o > C for 10 h; the mixture is transferred to an atmospheric distillation unit, and the solvent methanol is distilled off. The water was removed, and 120 g of a crude 1,2 pentanediol having a purity of 42.0% (gas chromatography, internal standard curve method of 1,2-propanediol internal standard) was filtered.

CLAIMS CN104926600

1.

The invention relates to a method for synthesizing 1,2-pentanediol by one-pot method, which is characterized in that 1-pentene, hydrogen peroxide and a catalyst are heated in a solvent to a certain temperature for a certain reaction.

2.

The hydrogen peroxide according to claim 1, characterized in that the hydrogen peroxide concentration is from 10% to 80% (w/w).

3.

The mass ratio of 1-pentene to hydrogen peroxide according to claim 1 or 2, characterized in that the ratio is 1:1 to 2.

4.

The catalyst according to claim 1, wherein the catalyst is titanium tetrachloride or a titanate having the formula of Ti(OR) 4 , and R is a C 1 - C 10 alkyl group.

5.

The catalyst according to claim 1 or 4, which is characterized in that the amount is from 0.1% to 10% (w/w) based on the mass of the raw material 1-pentene.

6.

The reaction temperature of claim 1 is characterized by a range of 10 < o > C-100 < o > C.

7.

The reaction temperature of claim 1 or claim 6 which is characterized by a constant temperature reaction.

8.

The reaction temperature of claim 1 or claim 6 characterized by a temperature programmed reaction.

9.

The reaction time described in claim 1 is from 1 h to 24 h.

10.

The solvent according to claim 1, wherein the solvent is one or a mixture of methanol, ethanol, isopropanol, n-butanol, acetone, methyl ethyl ketone, and dibutyl ketone.

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TITLE

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

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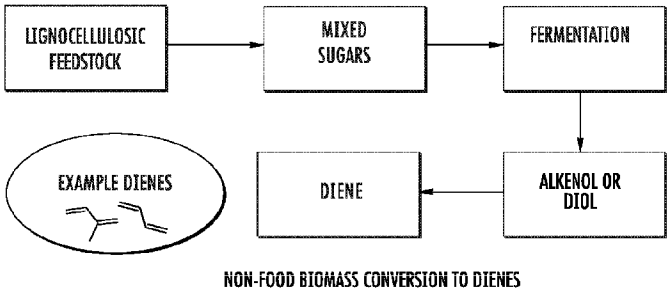

NON-FOOD BIOMASS CONVERSION TO DIENES

FIG. 1

(57) **Abstract**: The present invention relates to the fermentation of lignocellulosic sugars to afford crotyl alcohol that is then separated and converted to butadiene using a dehydration catalyst and a method and apparatus for converting alkenols or diols to dienes with high selectivity and conversion. The dienes are useful in preparing synthetic rubber, copolymers, and fuels.

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BIOMASS CONVERSION TO BUTADIENE

CROSS-REFERENCE TO RELATED APPLICATIONS

[01] This application claims the benefit of U.S. Provisional Application No. 62/021,651, filed on July 7, 2014, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[02] The invention generally relates to conversion of biomass to dienes, especially butadiene, by dehydration of alkenols or diols. The dienes, including butadiene, are useful in the preparation of synthetic rubbers, plastics, fuels, and additional chemical intermediates incorporated into valuable commercial products.

BACKGROUND

[03] The energy and cost-efficient conversion of non-food biomass to strategic chemical intermediates is one major step in securing a sustainable future. Lignocellulosic materials and the mixed sugars (C5 and C6) that can be obtained from this non-food source (*e.g.*, corn stover, a waste product from food production) are an ideal feedstock for anaerobic fermentations of certain bacteria. Of particular value are *Clostridium* species that possess a robust and naturally-occurring ability to ferment C5 and/or C6 sugars into many useful products.

[04] The acetone, butanol, and ethanol (ABE) biosynthetic pathways in *Clostridium* include well-established bio-catalytic steps where the key intermediates in the pathway are well-characterized (Fig. 8). Interestingly, in the *Clostridium* ABE process/pathway to bio-1-butanol, a key intermediate is crotonyl-CoA (Fig. 9).

[05] A number of renewable butadiene processes have been proposed. These include construction of metabolic pathways to produce butadiene or intermediates thereof in a host organism. This requires introduction of multiple exogenous polynucleotides encoding multiple enzymes into a host organism. This in turn requires subsequent optimization of the expression of the multiple introduced genes and co-optimization of the kinetic profiles of the expressed genes to maximize flow of substrate to product. This is very time-consuming and has a low probability of success. Moreover, host organisms that produce butadiene will require the design and deployment of new fermenter types, which is expensive and introduces additional risk. Therefore, there is a need in the art to develop strategies for

renewable butadiene production that require minimal genetic manipulation of a host organism, minimal additional capital expenditure and minimal risk.

[06] α-Olefins are useful intermediates in preparing dienes, including 1,3-butadiene, diesel and jet/turbine fuels, and polymers. 1-Butene is an especially useful precursor to 1,3-butadiene, which is used in preparing synthetic rubber and other useful polymeric elastomers. α-Olefins are also useful in preparing poly-α-olefins (PAOs) and copolymers with ethylene to form low-density plastics and elastomeric materials. Renewable α-olefins are useful in preparing the corresponding renewable products, including renewable fuels, polymers, elastomers, PAOs, and other chemical intermediates. Currently, the production of ethylene from natural gas is rapidly replacing the steam cracking of naphthas and as a consequence, the four-carbon feedstocks (byproducts like C4-raffinate, a mixture of butane, 1-butene, and 2-butenes) are rapidly shrinking in availability and rising in cost. Thus, the traditional source of petroleum-based and non-renewable C4-feedstock typically used for preparing butadiene is vanishing. It is this shortage of the petroleum feedstock that establishes a need for a renewable and sustainable pathway to butadiene.

[07] Obtaining α-olefins and dienes (*e.g.*, 1,3-butadiene) from renewable and sustainable resources requires a significantly different approach than currently used in petroleum processes. Since alcohols can be produced in large scale by fermentation processes, they are an attractive feedstock for α-olefin and diene preparations, provided they can be dehydrated at high conversion rates and with high selectivity. This requires achieving high selectivity in forming the alkene bonds and avoiding formation of carbon-oxygen double bonds (*i.e.*, ketones or aldehydes) or the cleavage of carbon-carbon single bonds.

[08] The conversion of oxygen-containing derivatives to butadiene has received considerable attention over the past seven-plus decades with several reviews written on the topic. One example is the article written by Egloff & Hulla [UOP, *Chem. Rev.* **1945**, *36(1)*, pp 63-141]. Perhaps the most outstanding results to date in fact go back to the work reported by Reppe et al. in 1943 [US patent **2310809**]. This work indicated that 1, 3-butanediol and/or 1, 4-butanediol could be doubly dehydrated over a combination of phosphoric acid, conjugate bases, and additional organic components to give butadiene in yields of greater than 90%. However, the WHSV is low relative to that acceptable for a viable industrial process and the lifetime of the catalyst is placed in weeks rather than years. The latter is a typical requirement for a viable commercial catalyst. Thus, there exists a need for a catalyst with sufficient activity, selectivity, and lifetime on stream.

[09] Over the last decade, work from the Sato laboratory at Chiba University, Japan has explored the dehydration of diols to alkenols, diols to butadiene, and the dehydration of alkenols to butadiene in significant detail. This work has focused on using inorganic oxide catalysts. One result of particular relevance is the work Ichikawa et al. reported [*J. Mol. Catal. A: Chem.* **2006**, *256*, pp 106-112] on the dehydration of petroleum-derived 2-buten-1-ol (*i.e.*, crotyl alcohol). The best inorganic oxide catalyst was based on a SiO_2-Al_2O_3 composition where the dehydration of crotyl alcohol gave a 76% conversion with a 93% selectivity (*i.e.*, 71% yield) (Fig. 10).

[10] Commercial production of bio-1-butanol has a rich history of successful large-scale production since the discovery by Louis Pasteur in 1861 of bacteria that could ferment sugars to a mixture of acetone, 1-butanol, and ethanol (ABE). Since Pasteur's initial discovery of the ABE process, many advances have been made in the fermentation process to optimize bio-1-butanol production and to reduce ethanol and acetone co-production. Most notable are the successful efforts using *Clostridium* bacteria in commercial plants that can produce bio-1-butanol at a cost competitive to and even less than current petroleum-derived 1-butanol.

[11] Since fermentations are carried out in aqueous medium, separation of the fermentation products of interest from the multi-component mixture ("fermentation broth") of water, bacteria, media components, and other metabolic byproducts is energy- and time-intensive. In the case of bio-1-butanol, several methods have been reported for isolating the butanol component. One method that has found commercial success is use of a sparging gas (*e.g.*, carbon dioxide or steam) that carries the more volatile bio-1-butanol/water azeotrope away from the fermentation broth. Other more academic approaches involve pervaporation. In these cases, a selective membrane material is used that permits bio-1-butanol to pass through, thus leaving the bacteria and water behind. Regardless of the method, it is evident to those skilled in the art that removing the last traces of impurities and water are costly in energy and time. The available methods vary significantly in capabilities. However, water and impurities are a direct and unavoidable consequence of bio-alcohol fermentation processing.

[12] Ruwet et al. (*Bull. Soc. Chim.* **1987**, *96*, pp 281-292) discuss the problems associated with using a wet ABE bio-1-butanol feed in a dehydration reaction to afford a mixture of olefins. More recently, D'Amore et al. (US2008/0015395 A1) reported extreme difficulty in dehydrating aqueous solutions of 1-butanol using a variety of acid catalysts to afford a mixture of olefins and other oxygenated products (*e.g.*, ethers),

including high amounts of unreacted 1-butanol. Improved methods are needed to dehydrate bio-alcohols, in particular methods for dehydration of wet bio-alkenols to bio-dienes.

[13] Other alternative catalysts include silica and alumina solid phase catalysts as well as standard mineral acid catalysts. D'Amore et al. (US2009/0030239) disclose the contact of water and alcohols with acid catalysts to afford a mixture of alkene products. Mixtures are typical of acid catalysis and previous work in the field discloses that complicated mixtures of alkene products are formed. The lack of regioselectivity for terminal olefin occurs when isomerization to the more thermodynamically stable internal olefin occurs. In some cases the internal olefins can be formed directly via an acid catalyzed mechanism, typically denoted as *E1*. These results clearly show that dehydration results can be severally complicated by the addition of water in acid-catalyzed dehydrations of bioalcohols.

[14] Internal alkenes are far less effective in Ziegler-Natta polymerization chemistry and are not of direct use in preparing high-flashpoint diesel and jet fuels and for making lubricants. Interestingly, butadiene can be an effective route to bio-1-butene by selective hydrogenation (Fig. 11).

[15] As a feedstock, it is highly desirable to have a selective process that affords rapid and high conversion to a terminal-olefin (*e.g.*, bio-1-butene) and is accompanied by no carbon skeletal rearrangement (*e.g.*, to isobutylene). Furthermore, bio-dienes such as bio-1,3-butadiene can be oligomerized/polymerized using a variety of sophisticated methods known in the art. Products prepared from butadiene are useful intermediates in forming reactive end-capped oligomers, lubricants, and fuels. 1,3-butadiene is also a useful intermediate for preparing several 6-carbon chemical intermediates useful in preparing polymers like nylon6,6 (Fig. 12).

BRIEF SUMMARY OF THE INVENTION

[16] Systems and methods are described for catalytic conversion of alkenols or diols to diene products. In some embodiments, the alkenol or diol reactant feed contains water. For example, the alkenol or diol may be produced in a microbial fermentation, and the feed for the catalytic conversion to diene may contain aqueous liquid from the fermentation medium.

[17] In some embodiments, a microorganism is engineered such that it produces crotyl alcohol from lignocellulosic biomass. In other embodiments, a non-engineered microorganism produces crotyl alcohol.

[18] In some embodiments, microbial production of crotyl alcohol is achieved through the deletion or inactivation of the bcd gene from a *Clostridium* organism (*e.g.*, which results

in stopping formation of butyryl-CoA). In some embodiments this is achieved through the ability of the native promiscuous alcohol dehydrogenase (adhE, adhe2) to convert crotonyl-CoA to crotonaldehyde. In some embodiments this is achieved through the ability of the native promiscuous alcohol dehydrogenases (adhE, adhE2, bdhAB) to convert the crotonaldehyde to crotyl alcohol. In some embodiments the production of crotyl alcohol from an engineered *Clostridium* is enhanced through treatment of the engineered *Clostridium* (*e.g.*, engineered to delete or inactivate the bcd gene) with one or more chemical mutagen followed by selection in the presence of conditions that bias the selection towards strains with increased crotyl alcohol production.

[19] A strategy is described herein whereby a microorganism which produces *n*-butanol is converted into a microorganism that produces crotyl alcohol, by deletion, inhibition, and/or inactivation of the activity of one, and possibly two, enzyme(s) (*e.g.*, bcd). With this microorganism, crotyl alcohol can be produced by fermentation using existing fermenter designs. Said crotyl alcohol can rapidly and inexpensively be converted to butadiene using a novel catalyst, also disclosed herein, thereby minimizing capital expenditure.

[20] Other strategies are described herein in which non-engineered microorganisms (e.g., microorganisms that produce *n*-butanol) may produce crotyl alcohol by adjustment of culture conditions to favor production of this product.

[21] In some embodiments, catalyst systems and processes are provided to convert alcohols (*e.g.*, bio-alcohols) to the corresponding dienes (*e.g.*, bio-dienes). In some embodiments, the alcohols (*e.g.*, bio-alcohols) described herein are alkenols (*e.g.*, bio-alkenols) or diols, which are converted to the corresponding dienes (*e.g.*, bio-dienes). In additional embodiments, alkenols (*e.g.*, bio-alkenols) are converted to the corresponding -α,ω-dienes (*e.g.*, bio-α,ω-dienes). In certain embodiments, 4-carbon alkenols (*e.g.*, bio-alkenols) are converted to 1,3-butadiene (*e.g.*, bio-1,3-butadiene). In specific embodiments, crotyl alcohol is converted to 1,3-butadiene. In some embodiments the feedstock (alcohol (*e.g.*, bio-alcohol), alkenol (*e.g.*, bio-alkenol), 4-carbon alkenol (*e.g.*, bio-alkenol), crotyl alcohol, or diol) contains from about 0.1 wt-% to about 90 wt-% water and, using systems and processes disclosed herein, delivers a product stream containing the corresponding diene (*e.g.*, bio-diene) and water. In some embodiments, the diene (*e.g.*, bio-diene) is produced with about 90% to about 99% chemical selectivity. In some embodiments, a single pass over the catalyst system affords a chemical conversion of greater than about 95%, about 98%, or about 99%. In some embodiments, the diene (*e.g.*, bio-diene) is

produced employing WHSV values greater than about 0.3 hr^{-1}, *e.g.*, greater than about 1 and less than about 10 h^{-1}, or about 0.3 hr^{-1} to about 10 hr^{-1}. In some embodiments of the methods disclosed herein, at least one solid phase catalyst is maintained at a temperature of about 200 °C to about 440 °C, or about 200 °C to about 320 °C, with the feed a solution containing alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) and water at a pressure of about 1 psig to about 1000 psig to produce a diene (*e.g.*, bio-diene) in high chemical selectivity at high alcohol conversion. In one embodiment, bio-crotyl alcohol that is obtained from a fermentation broth (*e.g.*, after removal of minor acidic contaminants) is dehydrated to bio-1, 3-butadiene in a yield of greater than about 80%, or greater than 85%, or greater than 90%.

[22] In one aspect, a method is provided for dehydrating an alkenol or a diol to a diene, including: contacting and heating the alkenol or diol with at least one catalyst that includes an inorganic support, one or more promoter(s) selected from one or more Group 1 element(s), one or more Group 2 element(s), and combinations thereof, and one or more buffer-adjusted anion(s) at a WHSV at least about 0.3 hr^{-1}, thereby producing a diene product that includes one or more diene(s) at a one-pass yield greater than about 72 mol%, or greater than about 73 mol%. In some embodiments, the WHSV is about 0.3 hr^{-1} to about 10 hr^{-1}. In some embodiments, the alkenol or diol is in a mixture with about 1 ppm to about 93 wt% water, or about 15 wt% to about 70 wt% water. In some embodiments, the selectivity of diene production is at least about 75%, at least about 80%, at least about 85%, at least about 90%, for example, greater than 95%, or about 90% to about 99%.

[23] In some embodiments, the alkenol is a bio-alkenol. In one embodiment, the alkenol is crotyl alcohol. In an embodiment, the crotyl alcohol is bio-crotyl alcohol. In some embodiments, the alkenol is a C_4 to C_6 alkenol. In some embodiments, 1,3-butadiene is produced in a method for dehydrating an alkenol or diol as disclosed herein.

[24] In some embodiments, the inorganic support includes γ-alumina, for example, in the form of an extrudate. In some embodiments, the catalyst is further modified with at least one organosilane, for example, an alkoxysilane, such as a chlorosilane.

[25] In some embodiments of the catalytic dehydration methods disclosed herein, at least one carrier gas is provided, for example, but not limited to, nitrogen and/or argon, or a mixture thereof.

[26] In some embodiments of the catalytic dehydration methods disclosed herein, heating is performed at a temperature of about 200° C to about 400° C. In some embodiments, the temperature is about 250° C to about 320° C.

[27] In some embodiments, the method further includes separating water from the diene product(s), thereby producing dry diene product(s).

[28] In some embodiments, the product of the dehydration reaction is 1,3-butadiene, and the method further includes contacting the 1,3-butadiene product with a second catalyst under conditions sufficient to produce 1-butene. In some embodiments, the 1-butene is contacted with a third catalyst, *e.g.*, a Ziegler-Natta catalyst, a mesoporous oligomerization catalyst, or an acid catalyst, under conditions sufficient to produce oligomers. In some embodiments, the oligomers are used to produce a fuel, *e.g.*, a diesel fuel or a jet fuel. In some embodiments, a diesel fuel is produced that has a flashpoint of about 38° C to about 100° C, a Cetane rating of about 45 to about 60, and aromatic content of less than about 0.5 wt-%. In some embodiment, a jet fuel is produced that has a flashpoint of about 38° C to about 100° C, a cold flow viscosity of less than about 8.0 cSt at -20 C, and aromatic content of less than about 0.5 wt-%.

[29] In some embodiments, the promoter(s) is(are) selected from Mg, Ca, Sr, Ba, and combinations thereof. In one embodiment, the promoter is Ca. In some embodiments, the buffer-adjusted anion is selected from SO_4^{-2}, $H_2PO_4^{-1}$, and mixtures thereof.

[30] In another aspect, a method is provided for dehydrating an alkenol or a diol to a diene, including: contacting and heating the alkenol or diol with at least one catalyst that includes a calcium-modified inorganic support and one or more buffer-adjusted anion(s), thereby producing a diene product that includes one or more diene(s) at a one-pass yield greater than about 80 mol%. In some embodiments, diene product(s) is(are) produced with greater than about 90 mol% selectivity and greater than about 90 mol% conversion. In some embodiments, the alkenol is a bio-alkenol. In one embodiment, the alkenol is crotyl alcohol, *e.g.*, bio-crotyl alcohol. In some embodiments the alkenol is a C_4 to C_6 alkenol. In some embodiments, the diene product is 1,3-butadiene. In some embodiments, the alkenol is in a mixture with about 1 ppm to about 93 wt-% water. In some embodiments, the contacting of the alkenol or diol with the at least one catalyst is performed at a WHSV of about 0.3 hr^{-1} to about 10 hr^{-1}. In some embodiments, the catalyst is modified by treatment with at least one organosilane.

[31] In another aspect, a method is provided for dehydrating crotyl alcohol to a diene product, including: contacting and heating the crotyl alcohol with at least one catalyst that includes an inorganic support, one or more promoter(s) selected from one or more Group 1 element(s), one or more Group 2 element(s), and combinations thereof, and one or more buffer-adjusted anion(s) at a WHSV at least about 0.3 hr^{-1}, thereby producing a diene

product that includes one or more diene(s) at a one-pass yield greater than about 73 mol%. In some embodiments, the Group 2 element is Ca. In some embodiments, the buffer-adjusted anion is selected from SO_4^{-2}, $H_2PO_4^{-1}$, and mixtures thereof. In some embodiments, the crotyl alcohol is in a mixture that includes about 1 ppm to about 93 wt-% water. In some embodiments, the mixture includes about 5 wt-% to about 70 wt-% water. In some embodiments, the crotyl alcohol is bio-crotyl alcohol. In some embodiments, the diene product is 1,3-butadiene. In some embodiments, the molar selectivity of diene production is greater than about 95%, about 90% to about 99%. In some embodiments, the inorganic support includes γ-alumina. In some embodiments, the catalyst is further modified by treatment with at least one organosilane, for example an alkoxysilane. In some embodiments, the method includes providing at least one carrier gas.

[32] In another aspect, catalyst compositions are provided herein for producing dienes from alkenols or diols with high selectivity, including: an inorganic support that is modified with at least one Group 1 element, at least one Group 2 element, or a combination thereof; one or more buffer-adjusted anion(s); and optionally, at least one organosilane. In some embodiments, the catalyst composition includes at least one Group 2 element selected from Mg, Ca, Sr, and Ba. In one embodiment, the Group 2 element is Ca. In some embodiments, the buffer-adjusted anion is selected from SO_4^{2-}, $H_2PO_4^{-1}$, and mixtures thereof. In some embodiment, the buffer-adjusted anion is $H_2PO_4^{-1}$, wherein $H_2PO_4^{-1}$ is a component of a mixture that further optionally includes one or more additional anions selected form HPO_4^{-2}, and PO_4^{-3}, and one or more additional charge balancing counter cations selected from H^+, Li^{+1}, Na^{+1}, K^{+1}, Mg^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2}, and combinations thereof. In some embodiments, the catalyst composition includes an organosilane, for example, diethoxydiphenylsilane. In some embodiments, the inorganic support includes γ-alumina, silica, titanium oxide, zinc oxide, zinc aluminate, or zirconium oxide.

[33] In some embodiments, catalyst compositions disclosed herein contain an inorganic support modified by a Ca^{+2} compound. In one embodiment, modification may be accomplished via treatment of the support with a mixture of calcium compounds, for example calcium bis(hydrogensulfate) and calcium sulfate, dissolved in a solvent. In some embodiments Ca^{+2} is the modifier and the Ca^{+2} compound is calcium bis(hydrogensulfate) [$Ca(HSO_4)_2$]. The solvent may be water, or an organic solvent, or a mixture of the two. In some embodiments, a solvent is used that is capable of completely dissolving the Ca^{+2} compounds used for preparation of the catalyst. In some embodiments, an "Incipient

Wetness Impregnation" (IWP) process is used for catalyst preparation. In one embodiment, the catalyst composition includes Ca^{+2} (as wt-% of the modified inorganic support) at about 0.8 to about 6.0 wt-%. In one embodiment, γ-alumina is used as the inorganic support. In some embodiments, γ-alumina is modified with binder, physically formed (*e.g.*, extruded) to a preselected shape (*e.g.*, rods), calcined, and then modified with a mixture of Ca^{+2} compounds as noted above in this paragraph. In some embodiments, calcium is preferred over Group 1 metals such as sodium and potassium when used at similar wt-% loading values.

[34] In one aspect, a method of making a catalyst composition described herein is provided. The method includes: a) modifying an inorganic support with at least one Group 2 element and at least one buffer-adjusted anion (e.g., a buffer mixture of anions) to produce a first modified inorganic support, wherein the first modified inorganic support includes the at least one Group 2 element and at least one buffer-adjusted anion; b) calcining the first modified inorganic support to produce a calcined first modified inorganic support; c) optionally contacting the calcined first modified inorganic support with at least one organosilane to produce a second modified inorganic support, wherein the second modified inorganic support includes the at least one Group 2 element, the at least one buffer-adjusted anion, and the at least one organosilane or a fragment thereof; and d) calcining the second modified inorganic support to produce the catalyst composition.

[35] In another aspect, a catalyst composition as described herein is provided, that is produced by a method that includes: a) modifying an inorganic support with at least one Group 2 element and at least one buffer-adjusted anion (*e.g.*, a buffer mixture of anions) to produce a first modified inorganic support, wherein the first modified inorganic support includes the at least one Group 2 element and at least one buffer-adjusted anion; b) calcining the first modified inorganic support to produce a calcined first modified inorganic support; c) optionally contacting the calcined first modified inorganic support with at least one organosilane to produce a second modified inorganic support, wherein the second modified inorganic support includes the at least one Group 2 element, the at least one buffer-adjusted anion, and the at least one organosilane or a fragment thereof; and d) calcining the second modified inorganic support to produce the catalyst composition.

[36] Promoter (*e.g.* Group 2 or Group 1 metal) modified and calcined catalysts may optionally be further modified by treatment with at least one organosilane to create new catalysts that are especially useful for the dehydration of alkenols (*e.g.*, bio-alkenols) or diols (*e.g.*, bio-diols) mixed with a high wt-% of steam. In some embodiments, buffer-

adjusted organosilane-modified catalysts afford high selectivity in forming diene (*e.g.*, bio-diene) products and can perform for extended periods of time on stream with little loss in selectivity.

[37] In some embodiments, methods disclosed herein for producing terminal olefins include using calcium or calcium-organosilane modified alumina catalysts, as described herein, for example, in isothermal continuous flow reactors or in a series of one or more adiabatic reactors. In some embodiments, some of the heat necessary for the dehydration reaction is carried into the reactor in the form of a gaseous diluent, such as steam. This creates a very water rich gas phase in the reactor making some embodiments of the methods disclosed herein beneficial for commercial applications.

[38] Some embodiments of the methods and systems described herein relate to fuels (*e.g.*, alternative and/or renewable fuels) and the production of dienes (*e.g.*, bio-dienes (*e.g.*, biodiesels)) that can be utilized to prepare a drop-in and full performance diesel fuel (*e.g.*, diesel biofuel), jet (*e.g.*, biojet) fuel, lubricant (*e.g.*, biolubricant), or other chemical products and/or intermediates useful in the production of commercial products.

[39] Embodiments also include such processes starting from cellulosic and/or hemicellulosic biomass material, as are shown schematically in FIG 1. Bio-alkenols or bio-diols can also be generated feeding a carbon-source of carbon dioxide and/or carbon monoxide to at least one biological organism. Typically the biological organism is suspended in water or it may be attached to at least one support system and then placed in contact with water and a carbon-source.

[40] In one aspect, methods are provided for dehydrating an alkenol (*e.g.*, bio-alkenol) to a diene (*e.g.*, bio-diene). In some embodiments, the method includes contacting and heating an alkenol (*e.g.*, bio-alkenol) with at least one catalyst that includes a calcium-modified (and optionally silanized) inorganic support at a WHSV of about 0.3 hr^{-1} to about 10 hr^{-1}, wherein the alkenol (*e.g.*, bio-alkenol) is in a mixture with about 1 ppm to about 93 wt% water, thereby producing the corresponding diene (*e.g.*, bio-diene) with greater than about 90% selectivity and greater than 98% conversion.

[41] In some embodiments of the methods disclosed herein, the alcohol (*e.g.*, bio-alcohol) is a C_4 to C_6 bio-alcohol. In one embodiment, the alcohol (*e.g.*, bio-alcohol) is butanediol (*e.g.*, 1,3-butanediol). The diene (*e.g.*, bio-diene) produced in some embodiments of the methods disclosed herein is 1, 3-butadiene. In some embodiments of the methods disclosed herein, the alcohol (*e.g.*, bio-alcohol) is a diol (*e.g.*, bio-diol) such as 2,3-butanediol or 1,3-butanediol.

[42] In some embodiments of the methods disclosed herein, the alcohol (*e.g.*, bio-alcohol) is an alkenol (*e.g.*, bio-alkenol) such as 2-butene-1-ol (*e.g.*, bio-2-buten-1-ol). For example, in some embodiments, the alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) may be a C_3 to C_{12} alcohol (*e.g.*, bioalcohol), *e.g.*, 1,12-decanediol (*e.g.*, bio-1,12-decanediol). The diene produced in some embodiments of the methods disclosed herein may be 1,3-butadiene (*e.g.*, bio-1,3-butadiene).

[43] In some embodiments of the methods disclosed herein, the 1-alkenol is an alcohol of general formula $R^1R^2CH=CHCH_2OH$, where R^1 and R^2 are independently H or a C_1 to C_{20} alkyl radical, or contain one or more aromatic rings containing exclusively carbon or a mixture of carbon and heteroatoms, or a nitrile, or an alkene, or a carboxylic acid, or ketone functional group, or a combination thereof.

[44] In some embodiments, the selectivity of diene (*e.g.*, bio-diene) production is greater than about 95%. In some embodiments, the selectivity of diene (*e.g.*, bio-diene) production is about 90% to about 99%. In some embodiments, the diene (*e.g.*, bio-diene) product includes ≤ about 5% unreacted 1-alcohol.

[45] In some embodiments, water is present in the feed reaction mixture at about 15 to about 70 wt%.

[46] In some embodiments, the inorganic support includes one or more phases of alumina (*e.g.*, γ-alumina), silica, titanium oxide, zirconium oxide, or zinc aluminate. In some embodiments, the inorganic support includes a combination of more than one of one or more phases of alumina, silica, titanium oxide, zirconium oxide, and zinc aluminate. The surface area of the inorganic support may be in the range of about 50 to about 400 m^2/g before modification and in the range of about 40 to about 440 m^2/g after modifications to form the catalyst.

[47] In some embodiments, the catalyst is further modified by treatment with at least one organosilane, for example, an alkoxysilane. In one embodiment, the organosilane is a chlorosilane. In one embodiment, the organosilane is diethoxydiphenylsilane. The organosilane may be dissolved in a solvent sufficient to form a homogeneous solution when combined with the organosilane and to wet the inorganic support.

[48] In some embodiments, the catalyst is further modified by treatment with at least one organosilane dissolved in an alcohol solvent. In some embodiments the alcohol solvent is *n*-propanol, 2-propanol, ethanol, or methanol. In one embodiment, the organosilane is diethoxydiphenylsilane and the alcohol solvent is ethanol. In another embodiment, the

organosilane is diethoxydiphenylsilane and the alcohol solvent is methanol. The alcohol solvent can contain from about 1 ppm water up to about 50 wt-% of the alcohol. For selected organosilane reagents with sufficient water solubility, water alone can be used to deliver the organosilane to the catalyst surface.

[49] In some embodiments of the methods of use of the catalysts, *e.g.*, for dehydration of alkenols or diols, at least one purge (*e.g.*, carrier) gas is provided, *e.g.*, nitrogen and/or argon.

[50] In some embodiments, the reaction mixture is heated to a temperature of about 200° C to about 440° C. In some embodiments, the temperature is about 260 °C to about 340 °C. In some embodiments, the temperature is about 250 °C to about 320 °C.

[51] In some embodiments, the method further includes separating water from 1, 3-butadiene product. In some embodiments, the method includes contacting the 1,3-butadiene product from which water has been removed with a second catalyst (hydrogenation type, *e.g.*, palladium on carbon) and hydrogen gas to form 1-butene (*e.g.*, bio-1-butene) in greater than 80% yield. Other more selective hydrogenation catalysts may also be used. The 1-butene (*e.g.*, bio-1-butene) is oligomerized with a third catalyst. In some embodiments, the third catalyst may be a Ziegler-Natta catalyst, a mesoporous oligomerization catalyst, or another catalyst that is capable of producing oligomers from dienes (*e.g.*, bio-dienes). In various embodiments, the oligomers may be used to produce a diesel fuel (*e.g.*, with a flashpoint of about 38 to about 100 °C, a Cetane rating of about 45 to about 60, and aromatic content of less than about 0.5 wt-%), a jet fuel (*e.g.*, with a flashpoint of about 38 to about 100 °C, a cold flow viscosity of less than about 8.0 cSt at -20 °C, and aromatic content of less than about 0.5 wt-%), or a lubricant (*e.g.*, with a viscosity of about 1 to about 10,000 cSt at 25 °C).

[52] In some embodiments, the method includes contacting and heating an alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) with at least one catalyst that includes a calcium-modified inorganic support and at least one buffer-mixture, thereby producing the corresponding diene (*e.g.*, bio-diene) with greater than about 90% selectivity and greater than about 90% conversion. Optionally, the alcohol (*e.g.*, bioalcohol) or diol (*e.g.*, bio-diol) is in a mixture with about 1 ppm to about 93 wt% water. Optionally, the catalyst is contacted with the alkenol at a WHSV of greater than 0.3 (*e.g.*, about 0.3 hr^{-1} to about 10 hr^{-1}). Optionally, the catalyst is further modified by treatment with at least one organosilane.

[53] In some embodiments, the method includes contacting and heating an alcohol (*e.g.*, bioalcohol, *e.g.*, alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol)) with at least one catalyst

that includes an inorganic support that is modified by a Group 2 element, an acid component, and at least one organosilane, thereby producing the corresponding diene with greater than about 90% selectivity. For example, the Group 2 element may include at least one of Mg, Ca, Ba, and Sr. Optionally, the alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) is in a mixture with about 1 ppm to about 93 wt% water. Optionally, the catalyst is contacted with an alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) at a WHSV of greater than 0.3 (*e.g.*, about 0.3 hr^{-1} to about 10 hr^{-1}). In some embodiments Group 1 metals can be used in place of Group 2 elements. This includes Li, Na, and K and mixtures of Group 1 and Group 2 metals can be used in one embodiment.

[54] In some embodiments, dehydration of crotyl alcohol (a bio-alkenol) using the catalyst compositions and methods described herein provides 1,3-butadiene (*e.g.*, bio-1,3-butadiene) in greater than 90% yield, and, in some embodiments, 90-99% selectivity for 1,3-butadiene or 95-99% selectivity. In some embodiments, the catalyst can be used continuously for at least 1 to 3 months, or about 6 months and in some embodiments, up to about 12 months, or up to about 18 months, or up to about 24 months or up to about 30 months, or about 36 months, or up to 48 months while producing -1,3-butadiene without significant loss in selectivity for the terminal diene.

[55] In another aspect, the charge of the Group 2 element is balanced with at least one counter anion (*i.e.*, X^-, where "X" represents a generalized counter anion, not limited to a halide ion) that is a component of the mixture of anions, and charge balancing counter cations, used for the buffer-adjustment. In some embodiments, the pKa for at least one respective conjugate acid (*i.e.*, XH) is in the range of about 0 to about 3, or about 1.5 to about 2.5. The composition of the Group 2 element may use a mixture of counter anions having one or more pKa values for each respective conjugate acid. In one embodiment then the Group 2 element is matched with counter anions that effectively form a buffer-adjusted surface on the inorganic support. For example, a mixture containing both $Ca(HSO_4)_2$ and $Ca(SO_4)$ can be used to deliver a buffered-adjusted promoter to the inorganic oxide surface. Another embodiment employs a mixture of phosphates (H_3PO_4, and counter anions $H_2PO_4^{-1}$, and HPO_4^{-2}, and/or PO_4^{-3}), when modifying with calcium or other Group 2 metals. In another embodiment the mixture of phosphates can be used with one or more Group 1 metal cation promoters. In some embodiments, the Group 2 or Group 1 metal is added to the inorganic oxide support in the amount of about 0.3 to about 4 wt-%, and buffering counter anions are used to balance the positive charge of the Group 1 and/or Group 2 cations selected.

[56] In one aspect, a method is provided for producing crotyl alcohol, including growing a microorganism in a growth medium under fermentation conditions suitable for production of crotyl alcohol. In some embodiments, the microorganism expresses one or more native enzyme(s) that can produce crotyl alcohol from a substrate in the growth medium and/or via a metabolic pathway in the microorganism. In some embodiments, the enzyme is an alcohol and/or aldehyde dehydrogenase. In some embodiments, the enzyme is an acyl-CoA reductase. In some embodiments, the substrate is crotonaldehyde. In some embodiments, crotyl alcohol is produced via a series of biosynthetic intermediates that include crotonic acid, crotonyl-CoA and/or other intermediates in the butanol/butanoate pathway. In some embodiments, the native enzyme(s) is(are) enzyme(s) in a native butanoate/butanol, fatty acid, amino acid degradation, or related metabolic pathway in the microorganism. In some embodiments, the metabolic pathway includes one or more of an enzyme of a glycolytic or pentose phosphate pathway that converts glucose and/or xylose to acetyl-CoA, a thiolase enzyme that converts acetyl-CoA to acaetoacetyl-CoA, a 3-hydroxy butyryl CoA dehydrogenase enzyme that converts acetoacetyl-CoA to 3-hydroxybutyryl-CoA, a crotonase enzyme that converts 3-hydroxybutyryl-CoA to crotonyl-CoA, an aldehyde dehydrogenase enzyme that converts crotonyl-CoA to crotonaldehyde, and an alcohol dehydrogenase enzyme that converts crotonaldehyde to crotyl alcohol. In some embodiments, the microorganism is engineered to produce crotyl alcohol or for improved crotyl alcohol production in comparison to the parent microorganism from which it is derived.

[57] In some embodiments, the microorganism is a *Clostridium* strain. In some embodiments, the *Clostridium* microorganism expresses an enzyme, *e.g.*, a native enzyme, that converts crotonaldehyde to crotyl alcohol, for example, an alcohol and/or aldehyde dehydrogenase. In some embodiments, the *Clostridium* microorganism expresses an enzyme, *e.g.*, a native enzyme, that converts crotonyl-CoA to crotonaldehyde or crotyl alcohol, for example, an acyl-CoA reductase, for example, that converts crotonyl-CoA to crotyl alcohol without additional intervening enzymatic activities.

[58] In some embodiments, the growth medium includes one or more substance(s) that increase production of crotyl alcohol in comparison to a growth medium that does not comprise the one or more substance(s). In some embodiment, the one or more substance(s) includes one or more co-factors of enzyme(s) in a butanoate/butanol metabolic pathway in the microorganism, *e.g.*, Mn, Fe, NADPH, and/or NADP. In some embodiments, the one or more substance(s) modifies (*e.g.*, activates or inhibits) the activity of one or more

enzyme(s), *e.g.*, one or more native enzyme(s), in the microorganism, thereby increasing crotyl alcohol production. In one embodiment bcd is inhibited by the one or more substance(s) in the growth medium. In one embodiment, adhE and/or adh2 are activated by the one or more substance(s) in the growth medium. In one embodiment, bcd is inhibited by one or more substance(s) in the growth medium and adhE and/or adh2 are activated by one or more substance(s) in the growth medium. In some embodiments, the one or more substance(s) in the growth medium includes one or more divalent metal ion(s) (*e.g.*, from selected from Ca, Co, Zn, and Mn, and combinations thereof), iodoacetamide, myristoyl-CoA, N-ethylmaleimide, and/or palmitoyl-CoA. In some embodiments, the growth medium comprises carbohydrate molecules produced by hydrolysis of lignocellulosic biomass.

[59] In one aspect, an engineered microorganism is provided that produces a greater amount of crotyl alcohol than the parent strain from which it was derived. In some embodiments, the microorganism is a genetically engineered *Clostridium* strain. In some embodiments, the microorganism (*e.g.*, *Clostridium* strain) has been engineered to comprise a reduced level or activity of butyryl-CoA dehydrogenase in comparison to the parent strain from which it was derived. In some embodiments, the microorganism (*e.g.*, *Clostridium* strain) includes overexpression of one or more enzyme(s) of a crotyl alcohol biosynthetic pathway. In some embodiments, the one or more enzyme(s) of crotyl alcohol biosynthesis includes one or more of an enzyme of a glycolytic or pentose phosphate pathway that converts glucose and/or xylose to acetyl-CoA, a thiolase enzyme that converts acetyl-CoA to acaetoacetyl-CoA, a 3-hydroxy butyryl CoA dehydrogenase enzyme that converts acetoacetyl-CoA to 3-hydroxybutyryl-CoA, a crotonase enzyme that converts 3-hydroxybutyryl-CoA to crotonyl-CoA, an aldehyde dehydrogenase enzyme that converts crotonyl-CoA to crotonaldehyde, and an alcohol dehydrogenase enzyme that converts crotonaldehyde to crotyl alcohol. In some embodiments, the one or more enzyme(s) of crotyl alcohol biosynthesis includes at least one alcohol dehydrogenase. In some embodiments, the microorganism (*e.g.*, *Clostridium* strain) is an SiHybrid in which butyryl-CoA dehydrogenase activity is downregulated in comparison to the parent strain from which it was derived. In some embodiments, the microorganism (*e.g.*, *Clostridium* strain) includes a butyryl-CoA dehydrogenase that has been inactivated using a targetron gene knockout system.

[60] In some embodiments, methods are provided for producing crotyl alcohol in an engineered microorganism, *e.g.*, genetically engineered microorganism, *e.g.*, engineered *Clostridium* strain, as described herein, including growing the microorganism in a growth

medium under fermentation conditions suitable for production of crotyl alcohol. In some embodiments, the growth medium includes carbohydrate molecules produced by hydrolysis of lignocellulosic biomass.

BRIEF DESCRIPTION OF THE DRAWINGS

[61] FIG. 1 illustrates an overall process for converting biomass to dienes

[62] FIG. 2 illustrates a high process flow diagram showing the preparation of a promoter and buffer-adjusted dehydration catalyst.

[63] FIG. 3 illustrates a high process flow diagram showing the preparation of a promoter and buffer-adjusted dehydration catalyst that is also silanized.

[64] FIG. 4 illustrates a high level process flow diagram showing the dehydration of an alkenol or diol using the promoter and buffer-adjusted dehydration catalyst in a single reactor system to afford a diene.

[65] FIG. 5 illustrates a high level process flow diagram showing the dehydration of an alkenol or diol using the promoter and buffer-adjusted dehydration catalyst in a two reactor system (i.e. adiabatic) to afford a diene.

[66] FIG. 6 illustrates the acid-catalyzed isomerization of crotyl alcohol to 3-buten-2-ol, and isomerization of 3-buten-2-ol to crotyl alcohol, and dehydration of both crotyl alcohol and 3-buten-2-ol to 1,3-butadiene.

[67] FIG. 7 illustrates a high level process diagram for the conversion of a four carbon alkenol or diol to six carbon monomers.

[68] FIG. 8 illustrates schematically catalytic dehydration of an alkenol to a diene.

[69] FIG. 9 illustrates the chemical structure of crotonyl-CoA.

[70] FIG. 10 illustrates schematically catalytic dehydration of crotyl alcohol to 1,3-butadiene.

[71] FIG. 11 illustrates schematically catalytic hydrogenation of 1,3-butadiene to 1-butene.

[72] FIG. 12 illustrates schematically conversion of 1,3-butadiene to other useful products.

[73] FIG. 13 illustrates schematically catalytic dehydration of an alkenol to a diene.

[74] FIG. 14 illustrates schematically catalytic dehydration of a diol to a diene.

[75] FIG. 15 shows the effect of crotyl alcohol addition on *n*-butanol production in *Clostridium* fermentations.

[76] FIG. 16 shows the effect of crotyl alcohol addition on *n*-butanol production in *Clostridium* fermentations.

[77] FIG. 17 shows the effect of crotyl alcohol addition on total solvent production in *Clostridium* fermentations.

[78] FIG. 18 shows the effect of crotonic acid addition on glucose consumption over time in *Clostridium* fermentations.

[79] FIG. 19 shows consumption of crotonic acid over time in *Clostridium* fermentations.

[80] FIG. 20 shows the effect of crotonic acid addition on *n*-butanol production over time in *Clostridium* fermentations.

[81] FIG. 21 illustrates schematically biosynthetic pathways in *Clostridium*.

[82] FIG. 22 illustrates schematically biosynthetic production of crotyl alcohol.

[83] FIG. 23 illustrates schematically a system for genetic engineering.

[84] FIG. 24 shows production of crotyl alcohol from crotonaldehyde in a butanol-producing *Clostridium* strain.

[85] FIG. 25 shows production of *n*-butanol with crotonaldehyde spiking at different concentrations in a butanol-producing *Clostridium* strain.

[86] FIG. 26 shows production of crotyl alcohol from crotonaldehyde in a butanol-producing *Clostridium* strain.

DETAILED DESCRIPTION

[87] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

[88] Methods and catalyst compositions are provided herein for conversion of alkenols (*e.g.*, bio-alkenols) or diols (*e.g.*, bio-diols) to dienes (*e.g.*, bio-dienes). In methods disclosed herein, an aqueous mixture (*e.g.*, a mixture that contains at least one alkenol or diol and water) is contacted with a solid phase catalyst, which produces a product stream containing a diene with high selectivity (*e.g.*, greater than about 90%) and an amount of water equal to the input water (*e.g.*, steam) plus the stoichiometric amount of water (*e.g.*, steam) produced from the dehydration reaction, shown schematically in Fig. 13.

[89] Typically, the catalytic reaction is performed at an elevated temperature (*e.g.*, from about 200 °C to about 440 °C). Catalysts that may be used in the methods described herein include but are not limited to Ca^{+2} modified inorganic supports, such as Ca^{+2}-modified γ-alumina, and can optionally include an organosilane component. Catalyst compositions for use in the methods herein typically include at least one acid component. In some embodiments, Ca^{+2} is present at about 0.8 to about 4.0 wt-% of the modified inorganic support.

[90] Catalyst systems and methods of use are provided that effect highly specific regioselective dehydration of alcohols (*e.g.*, bio-alcohols), *e.g.*, alkenols (*e.g.*, bio-alkenols) and diols (*e.g.*, bio-diols), in water-containing mixtures, with retention of selectivity over extended periods of use, commonly referred to as Time On Stream (TOS).

Definitions

[91] The terms "terminal alkene," "α-olefin," "terminal olefin," and "1-olefin" are used interchangeably herein to refer to an alkene with a double bond between the terminal carbon (carbon at the end of a hydrocarbon chain) and the adjacent carbon in the hydrocarbon chain.

[92] The terms "internal alkene," and "internal olefin," are used interchangeably herein to refer to an alkene which is not terminal, *i.e.*, the carbon-carbon double bond is not at the end of the hydrocarbon chain. A "2-alkene" is one example of an "internal alkene".

[93] A "diol," of which 1,3-butanediol is one example, refers to a molecule having two hydroxyl groups (alcohol functional groups) attached to different carbon atoms in the molecule. In one embodiment, a "bio-diol," *e.g.*, "bio-1,4-butanediol" is a diol that is biologically produced (*e.g.*, via a microbial fermentation process). In another embodiment, a "bio-diol," *e.g.*, "bio-1,3-butanediol" is a diol that is produced from a starting molecule that is biologically produced (*e.g.*, via a microbial fermentation process).

[94] A "diene," of which 1,3-butadiene is one example, refers to a molecule having two olefinic (carbon-carbon double) bonds. The olefinic bonds may be isolated (*e.g.*, as in 1,5-hexadiene), conjugated (*e.g.*, as in 1,3-butadiene), or adjacent (allenic, *e.g.*, as in 1,2-butadiene). In one embodiment, a "bio-diene," *e.g.*, "bio-1,3-butadiene" is a diene that is produced from a starting molecule (*e.g.*, an alkenol) that is biologically produced (*e.g.*, via a microbial fermentation process). In some embodiments, a bio-olefin, bio-diene, or biobutadiene is produced from a bio-alkenol that has been produced in a microbial

fermentation process from cellulosic biomass (*e.g.*, lignocellulosic biomass) as a starting material.

[95] A "1-alcohol" or "terminal alcohol" refers, interchangeably, to an alcohol with a hydroxyl group attached to a terminal, primary carbon in the hydrocarbon chain (*i.e.*, a $-CH_2OH$ group).

[96] "*n*-Butanol" and "*n*-propanol" refer, respectively, to 1-butanol and 1-propanol.

[97] "Bio-*n*-butanol" or "bio-1-butanol" refers to *n*-butanol that is produced biologically (*e.g.*, via microbial fermentation). In some embodiments, the bio-1-butanol is produced in a microbial fermentation process from cellulosic biomass (*e.g.*, lignocellulosic biomass) as a starting material.

[98] An "alkenol" refers to an olefinic alcohol, *i.e.*, a molecule containing at least one olefinic (carbon-carbon double) bond and at least one alcohol functional group. A "bio-alkenol" is produced biologically (*e.g.*, via microbial fermentation). In some embodiments, the bio-alkenol is produced in a microbial fermentation process from cellulosic biomass (*e.g.*, lignocellulosic biomass) as a starting material. For example 2-buten-1-ol, if derived from biomass, would be considered a bio-alkenol.

[99] 2-Buten-1-ol refers to crotyl alcohol. No assignment of double bond geometry or stereochemistry is assumed or implied. As used herein, "2-buten-1-ol" or "crotyl alcohol" refers to any/all of: *cis*-2-buten-1-ol (*Z*-2-buten-1-ol), *trans*-2-butene-1-ol (*E*-2-buten-1-ol), or/and the combination of *cis*- and *trans*-2-buten-1-ol in any proportion. In some embodiments "bio-2-buten-1-ol" or "bio-crotyl alcohol" refers to biologically produced bio-2-butene-1-ol (crotyl alcohol), *e.g.*, via microbial fermentation, including via microbial fermentation of biomass (*e.g.*, lignocellulosic biomass). In other embodiments "bio-2-buten-1-ol" or "bio-crotyl-alcohol" refers to crotyl alcohol that is produced by a chemical dehydration of a bio-diol that is first obtained from a microbial fermentation process from biomass (*e.g.*, lignocellulosic biomass) feedstock. For example, bio-1,3-butanediol can be dehydrated to form bio-2-buten-1-ol.

[100] For alpha-olefins, alkenes, alcohols, solvents, alkenols, bio-alkenols, and all chemical reagents used in descriptions within this document, IUPAC and/or standard organic chemical nomenclature accepted by the American Chemical Society (ACS) takes priority and is used to the best ability to match common nomenclature.

[101] "Biofuel," "biolubricant," or "bio-1,3-butadiene" refers to a fuel, a lubricant, or 1,3-butadiene, respectively, that is produced from at least one biologically-produced starting molecule or at least one starting molecule in which at least one carbon atom is derived from

a biological material, for example, cellulosic (*e.g.*, lignocellulosic) biomass. Also the direct biological conversion of carbon dioxide and/or carbon monoxide is considered also defined as a viable route to bio-alkenols or bio-diols. In one embodiment, a biofuel, biolubricant, or bio-1,3-butadiene may be produced from a bio-alkenol that is produced by a biological process as described herein.

[102] A "bio-" prefix is used to indicate a molecule or class of molecules, for example bio-alkenes or bio-alkenols, that are produced from at least one starting molecule in which at least one carbon atom is derived from a biological material, for example, cellulosic (*e.g.*, lignocellulosic) biomass.

[103] "Regioselectivity" refers to selective formation of one olefin product over another. For example, formation of 90 mol-% terminal (1-olefin) and 10 mol-% internal (*e.g.*, 2-olefin) would be described as 90% regioselectivity for the terminal olefin product.

[104] "Selectivity" refers to product selectivity if not otherwise defined.

[105] "Chemical Yield" and "Yield" refer to are calculated by multiplying the conversion (percent) by the selectivity (percent). For example, if reaction A that has a 90% conversion with a 90% selectivity for product X, then product X has a 81% yield in reaction A.

[106] "Incipient Wetness Impregnation" (IWP) is a technique that is used to modify a support material by treating the solid material with a predetermined amount of a solution containing at least one desired modifier (*e.g.*, calcium acetate), sufficient to wet the solid surface and fill the pore-volume, this followed by removal of some or all of the solvent (*e.g.*, by some method of evaporation) thus depositing the modifier uniformly on the support material.

[107] "Weight Hourly Space Velocity" (WHSV) is determined by dividing the weight of alcohol feed delivered per hour by the weight of catalyst used. For example, if 1.5 kg/hr of terminal alcohol are fed to a reactor containing 500 grams of catalyst, the WHSV is 3.0 hr^{-1}. The alcohol feed rate, in units of WHSV, as defined herein, is independent of the amount of water, or other components that may be in the feed, or co-fed to the catalyst bed.

[108] "Buffer-Adjusted Anions" refers to a mixture of anions in a pH buffer solution. For example a sulfuric acid buffer will contain HSO_4^{-1} and SO_4^{-2} anions as part of the buffer solution. The required cations are chosen in the process of making the buffer solution.

[109] "Ph" herein refers to a phenyl (C_6H_5-) group.

[110] "Me" herein refers to an methyl (CH_3-) group.

[111] "Et" herein refers to an ethyl (CH_3CH_2-) group.

[112] "Ac" herein refers to an acetate (CH_3COO-) group.

[113] "EFT X" in Figs. 24-26 refers to elapsed fermentation time of X hours.

Catalyst compositions and methods of preparation

[114] One embodiment for the dehydration catalysts disclosed herein is an inorganic support modified by contact with one or more promoter-containing compound(s), *e.g.*, a Ca^{2+}-containing compound. In one embodiment, a promoter (*e.g.*, a calcium-containing compound) is delivered as a solution to the inorganic support using incipient wetness impregnation. In another embodiment, a promoter (*e.g.*, a calcium-containing compound) is delivered by spraying a promoter-containing (*e.g.*, calcium compound-containing) solution onto an inorganic support while the latter is carried on a belt system or is mixed in a rotating drum. In a further embodiment, vapor phase deposition is used to deposit promoter(s) on an inorganic support. Solvents used to prepare the promoter solution may be aqueous, or one or more organic solvent(s), or a mixture thereof. Nonlimiting examples of calcium-containing compounds that may be used for production of the catalysts described herein include $Ca(SO_4)$, $Ca(HSO_4)_2$, $Ca_3(PO_4)_2$, $Ca(HPO_4)$, or $Ca(H_2PO_4)_2$, any one of which may be available and used in more hydrated, or more dehydrated, or more condensed forms, than suggested by the chemical formulas cited here. Other calcium and Group 2 compounds, or Group 1 compounds, or Group 3 compounds, or Group 4 compounds, or rare earth compounds may be employed for this purpose as promoters.

[115] In addition to one or more promoter(s), the catalyst compositions disclosed herein include one or more "Buffer-Adjusted Anion(s)" (BAA). The selected anion, or mixture of anions, incorporated into the catalyst with the chosen promoter or mixture of promoters, improves the selectivity of the dehydration. The counter cations that accompany one or more BAA may include promoter(s) that are advantageous for the dehydration reaction, for example Ca^{+2}, or they can include a mixture of solely Group 2 or solely Group 1 metal cations, or a mixture of both Group 1 and Group 2 ions. In some embodiments, the BAA includes phosphate-containing ions or sulfate-containing ions, which have a well-established history of use in preparing aqueous buffer solutions. Nonlimiting examples of BAA include sulfate (SO_4^{-2}) and dihydrogenphosphate ($H_2PO_4^{-1}$) anions.

[116] In another embodiment, BAA is added as counter anion to the promoter using at least one Group 1 or Group 2 metal counter cation, in which case provision is also made to provide a buffering quantity of the conjugate acid of the BAA. For example, where the BAA is dihydrogenphosphate ($H_2PO_4^{-1}$), the conjugate acid (H_3PO_4), is also supplied, as exemplified by "Catalyst 4," described in Example 10, *infra*. The promoter metal ion

concentration may be maintained at about 0.5 wt-% to about 4 wt-% of the inorganic (*e.g.*, oxide) support. Suitable BAA include those anions wherein the pKa of the conjugate acid of the BAA falls in the range of zero to about 3. One non-limiting example of a suitable BAA for this embodiment is sulfate ion, whose conjugate acid, hydrogen sulfate ion (HSO_4^{-1}), has a pKa of about 2, between zero and about 3. Having selected SO_4^{-2} according to the criterion that the pKa of the conjugate acid falls within the range of zero to about 3, the conjugate acid (HSO_4^{-1}), and the corresponding free acid (H_2SO_4), in combination with the selected anion(s), may be used to prepare the catalyst.

[117] The BAA may be delivered I the form of its conjugate acid. For example, in a catalyst where sulfate (SO_4^{-2}) is among the selected BAA(s), the catalyst may be formulated using $NaHSO_4$ (where HSO_4^{-1} is the conjugate acid of SO_4^{-2}), as in "Catalyst 2," described in Example 8, *infra*. Regardless, for a selected BAA, the catalyst is formulated using a source of the conjugate acid of the BAA, or another acid with a pK1 within the range of zero to about 3. For example, in the case that the selected BAA is SO_4^{-2}, a source of the conjugate acid, HSO_4^{-1}, may be supplied, or H_3PO_4, another acid with a pKa within the range zero to about 3, may be supplied. The conjugate acid of the BAA may be supplied directly, or by a suitable combination of anions, and corresponding charge balancing cations. For example, where the BAA is SO_4^{2-}, the conjugate acid may be delivered directly as a HSO_4^{-1} salt (including Group 1 or Group 2 elements, such as $NaHSO_4$ or $Ca(HSO_4)_2$), or by a combination of H_2SO_4 and a SO_4^{2-} salt (including Group 1 or Group 2 elements, such as Li_2SO_4 or $CaSO_4$).

[118] In some embodiments the free-acid, for example, H_3PO_4 or H2SO4, is added as part of the BAA solution. Further, it is understood that, depending upon several factors, including the relative ratios of selected BAAs, the relative amounts of selected promotors, the surface properties of the selected inorganic support, and the composition of the diol or alkenol feed to the dehydration catalyst, during catalyst operation a portion of the BAAs present in the original catalyst formulation may be present as the corresponding free acid, *i.e.*, the counter cation(s) will be protons (H^+ ions). There is no requirement that all the BAAs, or their corresponding conjugate acids, are charge-balanced exclusively by promotor cations, either in the catalyst as-synthesized, as-formulated, as-charged to the dehydration reactor, or in-use. For example, even though the BAA SO_4^{-2} ion may be delivered using the sodium salt of the conjugate acid, HSO_4^{-1} ($NaHSO_4$), as described above, in which case the counter cation is a promoter (Group 1), alternatively the HSO_4^{-1} may be delivered as H_2SO_4 or $(NH_4)HSO_4$. It is understood and expected that a portion of the BAAs may be effectively

present in the buffered catalyst as the corresponding free acid, *e.g.*, H_2SO_4, if HSO_4^{-1} or SO_4^{-2} are among the anions in the catalyst formulation.

[119] In one embodiment of a catalyst composition disclosed herein, the inorganic support is γ–alumina, the Group I element is Na, the buffer-adjusted anion is sulfate (SO_4^{-2}), and the catalyst is formulated using the sodium salt of the conjugate acid of the buffer-adjusted anion, $NaHSO_4$.

[120] In one embodiment of a catalyst composition disclosed herein, the inorganic support is γ -alumina, the Group 2 element is Ca, the buffer-adjusted anion is dihydrogenphosphate ($H_2PO_4^{-1}$), and the catalyst is formulated using a mixture of the Ca salt of the buffer-adjusted anion [$Ca(H_2PO_4^{-1})_2xH_2O$] and the conjugate acid of the buffer-adjusted anion (H_3PO_4).

[121] In one embodiment of a catalyst composition disclosed herein, the inorganic support is γ -alumina, the Group 2 element is Ca, the buffer-adjusted anion is dihydrogenphosphate ($H_2PO_4^{-1}$), the catalyst is formulated using a mixture of the Ca salt of the buffer-adjusted anion [$Ca(H_2PO_4^{-1})_2xH_2O$] and the conjugate acid of the buffer-adjusted anion (H_3PO_4), and organosilane is diethoxydiphenylsilane, delivered to the catalyst from a solution in ethanol.

[122] In some embodiments, a promoter (*e.g.*, Ca^{+2}) buffer-adjusted mixture is dissolved in one or more solvent(s) to create a solution, the promoter (*e.g.*, Ca^{+2}) solution is placed in contact with the carrier (*e.g.*, ϒ-alumina), and the solvent(s) is (are) then removed, *e.g.*, with heat and/or reduced pressure. Those experienced in the methods of surface modification know that one technique to accomplish this is referred to as incipient wetness impregnation (IWP). IWP is typically followed by a calcination process of some time, as shown schematically in FIG 2. The inorganic support (**200**) is added to vessel **201** and then addition of the IWP solution **202**, which includes promoter (*e.g.*, Ca^{2+}) and BAA, is done in such a way as to provide even distribution. This can be done, for example, by adding solution **202** by a spraying method. Mechanical mixing in apparatus **203** can also be used facilitate even distribution of the promoter solution. The wetted material in **203** is then heated to remove some or all of the IWP solvent. This material **204** can be further heated in a second apparatus (**205**) to provide calcination of the catalyst. The calcination can be carried out in vessel **203** or **205** at temperatures of about 100 °C to about 900 °C, or about 200 °C to 600 °C, for a time period of about 1 hour to about 8 hours, or about 2 hours to 6 hours. The removal of the solvent can be done in air or under an inert atmosphere. In one embodiment the wetting solution is removed under a reduced pressure. The catalyst

removed from **203** or **205** can be sized by sifting or other methods common to solid phase catalyst processing, thus producing finished catalyst **206**. The concentration of Ca^{+2} in the solution is predetermined in such a way that a targeted amount of Ca^{+2} is deposited on the carrier (*e.g.*, alumina) surface. In some embodiments, the Ca^{+2} is deposited in the range of about 0.8 wt-% to about 4.0 wt-% or about 1.0 wt-% to 1.7 wt-% of the total catalyst {weight of Ca^{+2}/(weight of inorganic support + weight of Ca^{+2}) x 100 = wt-%}. Delivery of the calcium and the buffer-adjusted anions can also be made using other techniques such as, non-IW impregnation or, for example, vapor deposition followed by calcination in air or under an inert atmosphere. In some embodiments, all of the modifications are carried out on the final shape or sized support material.

[123] In some embodiments, the promoter-doped (*e.g.*, Ca^{+2}) and buffer-adjusted inorganic support (*e.g.*, γ-alumina) can be further modified by treatment with one or more organosilane(s). Treatment with organosilane(s) may provide a catalyst with improved stability for the dehydration of alcohols. In some embodiments, the organosilane(s) can be delivered to the inorganic support (*e.g.*, a Ca^{+2} and buffer-adjusted modified γ-alumina carrier) using IWP, as shown in a high level and general view in FIG 3. In this embodiment the calcium-modified buffer-adjusted inorganic support **206** is treated with the IWP solution **301** in such a way as to provide even distribution. This can be accomplished by spraying the organosilane(s) or a solution containing organosilane(s) **301** while mechanically mixing the promoted carrier in vessel **302**. The mixing process can greatly facilitate achieving an even distribution of the organosilane(s). However, it is not always necessary. The wetted material in apparatus **302** is then heated to remove some or all of the IWP solution and/or can be transferred to vessel **303** for further drying under ambient or reduced pressure. The catalyst (**304**) can be formulated, shaped, and sized by sifting or other methods common to solid phase catalyst processing. In one embodiment, a shaped or sized support (*e.g.*, **206**) may be used in the modification process, hence providing the catalyst **304** in an advantageous physical state (*e.g.*, shape or particle distribution).

[124] An organosilane solution **301** used to modify the carrier, *e.g.*, by IWP, can be made using water, one or more organic solvent(s), or a mixture of water and organic solvent(s) with or without additional additives. In one embodiment, the solvent is selected so that sufficient organosilane is soluble in the chosen solvent to deliver the required amount of organosilane to the solid by incipient wetness. Typical concentration of organosilane(s) when used in a IWP solvent is about 0.05 wt-% to about 4 wt-%, about 0.1 wt-% to about 0.2 wt-%, about 0.15 wt-% to 1.5 wt-%, or 0.3 wt-% to 1.3 wt-% total organosilane

concentration. In another embodiment, the organosilane(s) can be delivered in neat form, for example, as a liquid or in the vapor phase. Contact time for the neat organosilane(s) or organosilane-IWP solution with modified carrier may be about 5 minutes to about 6 hours, about 1 hour to about 6 hours, or about 2 hours to about 4 hours, thus allowing for complete dispersion and reaction, at or about ambient temperature (*e.g.*, about 20 °C to about 30 °C). Solvent(s) removal may be accomplished by the application of heat and/or reduced pressure. The typical final temperature reached is about 40 ° C to about 200 °C, about 300 °C, or about 400 °C. Removal of the solvent(s), if used, can be done in air or under an inert atmosphere (*e.g.*, nitrogen or argon).

[125] Typical organosilanes for use in the catalyst preparation methods disclosed herein include, but are not limited to, chlorosilanes, for example, Ph_2SiCl_2 and Ph_3SiCl. In some embodiments, alkoxysilanes may be used. For example, organosilanes such as Ph_3SiOEt and $Ph_2Si(OEt)_2$ can also be used to create a silanized-dehydration catalyst. Furthermore, R_3SiX, R_2SiX_2, and $RSiX_3$ organosilanes can be used, where R is a mixture of aryl and alkyl radicals and X represents a leaving group. The R-groups can be the same or a combination of alkyl, aryl, or organic functionalized substituents. Typical leaving groups include, but are not limited to, halide, alkyl carboxylate (*e.g.*, acetate), alkoxy (*e.g.* methoxy), or alkyl di- (*e.g.*, oxalate) and tri-carboxylates (*e.g.*, citrate).

[126] In some embodiments, water soluble organosilane(s) are employed in the silanization process (*e.g.*, treatment of the support with an organosilane solution and calcining). For these embodiments, the organosilane(s) may be soluble in water, for example, at levels of up to about 3 wt-%. The water solubility can be achieved by the use of hydrogen bonding groups attached to the silicon atom [*e.g.* $PhSi(OH)_3$] or by incorporation of a hydrogen bonding group or a dipolar functional group to one or more of the groups attached to the silicon atom. Examples could include, but are not limited to, an alkyl amine, ether, epoxide, or other dipolar or hydrogen bonding functional groups. In some embodiments, solubility of the organosilane(s) can be increased by heating a water solution to at least about 40 °C, about 50 °C, about 60 °C, or about 90 °C.

[127] The effect and benefit of silanization is dependent upon the carrier used, alkenol or diol feed, and the wt-% of water content added or contained in the alcohol feed. Typically, reaction conditions employing high water concentrations (*e.g.*, >50 wt-%) in the feed may exhibit the greatest benefit from silanization of the catalyst and afford very stable dehydration catalysts. Silanization of calcium promoted, or Group 1, or Group 2, or other promoted modified aluminas provides a catalyst that provides enhanced stability, which is

reflected in retention of selective diene (*e.g.*, bio-diene) production as disclosed herein. The process of silanization can be applied to aluminas (*e.g.*, γ-alumina) or other inorganic supports (*e.g.*, zinc aluminate) modified with Group 3, or Group 4, or Group 5, or Group 6, or Group 7, or Group 8, or Group 9, or Group 10 metals.

[128] Catalyst products **206** and **304** may be left as powders, for example, in the range of about 10 to about 1000 microns, or about 50 to about 200 microns, or they can be pelletized or shaped using techniques common to those skilled in the art. In some embodiments, pellets and shaped particles may provide advantages in controlling the pressure drop across the catalyst reactor bed. This may be important where physical process requirements require long reaction tubes or where low head-pressures are desirable. Pellets may be any shape or size. In some embodiments, pellet diameters are about 1/16 inch to about ¼ inch, with lengths about 1 to about 10 times the diameter, or about 2 to about 4 times the diameter. One embodiment includes first shaping, or pelletizing, or crushing with size selection (*e.g.* sieving), of the support, followed by the addition of at least one promoter as described herein.

Dehydration Methods

[129] The catalyst compositions described herein may be used to dehydrate alkenols (*e.g.*, bio-alkenols) or diols (*e.g.*, bio-diols), to produce diene (*e.g.*, bio-diene) products. In one embodiment, catalyst compositions disclosed herein may be used to dehydrate crotyl alcohol (*e.g.*, bio-crotyl alcohol) to 1,3-butadiene (*e.g.*, 1,3-bio-butadiene). In some embodiments, the catalyst compositions disclosed herein may be used to dehydrate alkenols or diols in the presence of water.

[130] In methods for dehydration of a alkenol or diol using the catalyst compositions disclosed herein, the water content in the initial alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) mixture (alkenol-water or diol-water mixture) that is fed to the catalyst can be from about 0.1 wt-% to about 93 wt-%, about 1 wt-% to about 70 wt-%, about 10 wt-% to about 50 wt-%, about 15 wt-% to about 19 wt-%, or about 17 wt-%. The water in the alkenol or diol feed can be contained in an alkenol-water mixture or diol-water mixture, or added using a second and separate feed, or may be a combination of the two {*e.g.*, total water in feed = (alkenol or diol + water mixture) + water feed}. In some embodiments, additional water is added to the alkenol-water or diol-water mixture prior to contact with the catalyst, thereby producing an alkenol or diol feed that contains about 30 wt-% to about 93 wt-% of water, or about 45 wt-% to about 70 wt-% of water. The use of high water content in the alkenol or

diol feed is especially well tolerated with catalysts prepared as disclosed herein. In some embodiments, the alkenol or diol feed in contact with the catalyst (*e.g.*, optionally including additional water added to the alkenol-water or diol-water mixture prior to entering the reactor and/or water added separately into the reactor) includes about 1 wt-% to about 70 wt-% water for optimum production of diene (*e.g.*, bio-diene), *e.g.*, 1,3-butadiene (*e.g.*, bio-1, 3-butadiene). In some embodiments, the alkenol or diol feed includes >90 wt-% water. In some embodiments, the water content in the alkenol or diol feed is about 1, about 5, about 10, about 15, about 20, about 25, about 30, about 35, about 40, about 45, about 50, about 55, about 60, about 65, about 70, about 75, about 80, about 85, or about 93 wt-% or more. In some embodiments, the water content in the alkenol or diol feed is about 15 to about 20 wt-%, about 15 to about 70 wt-%, or about 50 to about 80 wt-%. The diene (*e.g.*, bio-diene) product stream of the reaction may contain an amount of water as described above in this paragraph (*e.g.*, about 0.1 wt-% to about 93 wt-%), or values or subranges described above that are greater than the stoichiometric amount of water that is produced in the dehydration reaction.

[131] Catalysts disclosed herein may dehydrate wet alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) mixtures that contain large amounts of water. In some embodiments, steam may be added prior to contact with the catalyst to afford high selectivity for the diene (*e.g.*, bio-diene) dehydration product. Furthermore, in some embodiments, a high selectivity may be maintained for extended periods of time on stream, for example, about 1 month to about 3 months, about 6 months, about 12 months, about 18 months, about 24 months, about 30 months, about 36 months, about 42 months, about 48 months, or longer.

[132] Catalysts disclosed herein may also dehydrate an alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) mixture that contains water at levels as low as 1 ppm to 1000 ppm where equal performance of catalyst to afford diene (*e.g.*, bio-diene) product is observed throughout the entire range of low water content and the catalyst can maintain high selectivity for extended periods of time on stream, for example, about 1 month to about 3 months, about 6 months, about 12 months, about 18 months, about 24 months, about 30 months, about 36 months, about 42 months, about 48 months, or longer.

[133] In one embodiment of a method for dehydrating an alkenol or diol to a diene as described herein, the alkenol is crotyl alcohol, the diene is 1,3-butadiene, the inorganic support is γ-alumina, the Group 1 element is Na, the buffer-adjusted anion is sulfate (SO_4^{2-}),

and the catalyst is formulated using the sodium salt of the conjugate acid of the buffer-adjusted anion, $NaHSO_4$.

[134] In one embodiment of a method for dehydrating an alkenol or diol to a diene as described herein, the alkenol is crotyl alcohol, the diene is 1,3-butadiene, the inorganic support is γ -alumina, the Group 2 element is Ca, the buffer-adjusted anion is dihydrogenphosphate ($H_2PO_4^{-1}$), and the catalyst is formulated using a mixture of the Ca salt of the buffer-adjusted anion [$Ca(H_2PO_4^{-1})_2xH_2O$] and the conjugate acid of the buffer-adjusted anion (H_3PO_4).

[135] In one embodiment of a method for dehydrating an alkenol or diol to a diene as described herein, the alkenol is crotyl alcohol, the diene is 1,3-butadiene, the inorganic support is γ -alumina, the Group 2 element is Ca, the buffer-adjusted anion is dihydrogenphosphate ($H_2PO_4^{-1}$), the catalyst is formulated using a mixture of the Ca salt of the buffer-adjusted anion [$Ca(H_2PO_4^{-1})_2xH_2O$] and the conjugate acid of the buffer-adjusted anion (H_3PO_4), and organosilatne is diethoxydiphenylsilane, delivered to the catalyst from a solution in ethanol.

[136] An example of a catalytic alkenol or diol dehydration process as disclosed herein is shown schematically in FIG 4. An alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) feed **400** is introduced to the vaporization/mixing vessel (**401**) to which a water feed is added at some preselected amount. The output of **401** is transferred to vessel **403,** which contains the dehydration catalyst (*e.g.*, **206** or **304** prepared above) at an elevated temperature, for example, about 200 °C to about 440 °C, or about 250 °C to about 420 °C. Optionally, a purge (*e.g.*, carrier) gas, *e.g.*, an inert gas such as argon and/or nitrogen, may used to control dwell time in the reactor chamber. Temperature may be modified to optimize diene (*e.g.*, bio-diene), *e.g.*, 1,3-butadiene *(e.g.*, bio-1,3-butadiene), production for a particular alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) feedstock. In some embodiments, the rate of alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) feedstock passage is about 0.3 to about 10 mass units of feedstock per mass unit of catalyst/h (*i.e.*, 0.3 to 10 WHSV), or about 1.2 to about 2.0 WHSV, or may be greater than about 1 and less than about 6 WHSV in some embodiments. In some embodiments, water content in the alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) feedstock in contact with the catalyst in the reactor **403** (water in the alcohol (alkenol or diol) feed entering the reactor, and optionally additional water added to the feed and/or added separately into the reactor) is about 1 ppm *(i.e.*, 0.0001 wt-%) to about 93 wt-%. The output from apparatus **403** is fed to a cooling/condenser system **404**. The output

from **404** is transferred to a decanter where an aqueous solution **407** separates from the diene product **405**. The isolated water product **407** (after decanting or distillation to create the isolated alkene **406**) may be optionally passed through a filter material, and/or one or more other unit operations **408** to remove traces of organic acids or other unwanted byproducts that may be produced during the dehydration reaction, thereby producing a purified water stream **402**. Optionally, the water stream **402** may be added to the alkenol or diol feed in **401**.

[137] In some embodiments, the alcohols (*e.g.*, bio-alcohols) (alkenols (*e.g.*, bio-alkenols) or diols (*e.g.*, bio-diols)) that may be selectively dehydrated to produce dienes (*e.g.*, bio-dienes) with the catalyst compositions and methods disclosed herein may include at least one additional organic functional group. Non-limiting examples of such organic functional groups include, but are not limited to, aromatic (*e.g.*, with an aromatic ring that consists of carbon atoms or contains a mixture of carbon and heteroatoms), nitrile, alkene, or ketone functional groups. In some embodiments, the alcohol is a terminal alcohol. In other embodiments, the alcohol is not a terminal alcohol (*e.g.*, 2,3-butanediol).

[138] In some embodiments, diols are used in the dehydration methods disclosed herein. Nonlimiting examples include 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1,4-pentanediol, 1,3-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 1,5-hexandiol, 2,4-hexanediol, 1,3-hexanediol. In one embodiment, an aqueous solution of 1,3-butanediol (*e.g.*, containing from about 5 to about 95 wt-% of the diol) is dehydrated in a double dehydration to afford 1,3-butadiene, shown schematically in Fig. 14.

[139] In some embodiments, alkenols are used in the dehydration methods disclosed herein. A nonlimiting example is 2-butene-1-ol. In some embodiments of the methods disclosed herein, the 1-alkenol is an alcohol of general formula $R^1R^2CH{=}CHCH_2OH$, where R^1 and R^2 are independently H or a C_1 to C_{20} alkyl radical, or contain one or more aromatic rings containing exclusively carbon or a mixture of carbon and heteroatoms, or a nitrile, or an alkene, or a carboxylic acid, or ketone functional group, or a combination thereof.

[140] In some embodiments, the alkenol or diol may be a C_3 to C_{12} alcohol, *e.g.*, 1,12-decanediol.

[141] The diene produced in some embodiments of the methods disclosed herein may be 1,3-butadiene (*e.g.*, bio-1,3-butadiene).

[142] The input steam may be useful in double dehydration reactions that form a terminal olefin that is in conjugation with a second olefin bond (e.g. 1, 3-butadiene). Conjugated

dienes are generally more reactive and thus less stable. Dilution with solvent is commonly used to slow their decomposition/polymerization chemistry.

[143] In some embodiments of the dehydration methods disclosed herein, the alkenol or diol and water are heated to about 200 °C to 400 °C and then contacted with the dehydration catalyst. In some embodiments, the alkenol is crotyl alcohol. In one embodiment, the catalyst is "**Catalyst 2**," described *infra* in Example 8. In one embodiment, the catalyst is "**Catalyst 2**," described *infra* in Example 8, and the alkenol is crotyl alcohol. In one embodiment, the catalyst is "**Catalyst 4**," described *infra* in Example 10. In one embodiment, the catalyst is "**Catalyst 4**," described *infra* in Example 10, and the alkenol is crotyl alcohol. In one embodiment, the catalyst is "**Catalyst 5**," described *infra* in Example 12. In one embodiment, the catalyst is "**Catalyst 5**," described *infra* in Example 12, and the alkenol is crotyl alcohol. The exiting product stream may be at a temperature of about 150 °C to about 350 °C. In embodiments of the dehydration methods disclosed herein, the final product stream may contain about 10 mol% alkenol or diol or less (based on alkenol or diol fed; corresponding to about 90 mol%, or greater, alkenol or diol conversion), about 5 mol% alkenol or diol or less (based on alkenol or diol fed; corresponding to about 95mol%, or greater, alkenol or diol conversion), or less than about 0.5 mol% alkenol or diol (based on alkenol or diol fed; corresponding o about 99.5 mol%, or greater, alkenol or diol conversion). Embodiments of the methods disclosed herein may produce the diene product with about 90% to about 98% or greater selectivity for the diene.

[144] The alkenol or diol dehydration methods disclosed herein may be operated in either isothermal or adiabatic configurations.

[145] In a further embodiment, the dehydration method may include at least two reactors in sequence, with the same, similar, or better performance and yield as the single reactor system. Having the catalyst in more than one reactor can eliminate the need for external heating of the commercial reactors. Heating large commercial reactors in an isothermal manner can be cost prohibitive. In some embodiments, the product stream from the catalytic dehydration reaction (*e.g.*, **403**) is then heated again to about 200 °C to about 400 °C and contacted with a second reaction vessel containing dehydration catalyst. An example of a two-reactor process is shown schematically in FIG 5. The alkenol or diol feed **500** is added to the vaporization/mixing vessel **501** and a water feed is also added at some preselected amount. The output of **501** is transferred to the first catalyst vessel **503** which contains the dehydration catalyst (*e.g.*, **206** or **304**, prepared as described above). The output from **503** is reheated in inter-stage heater **504** and fed to a second catalyst vessel **505**.

Vessel **503** and **505** typically do not have an external source of heat applied. The product stream from **505** is taken to a cooling/condenser system **506**. The output from **506** is transferred to a decanter where an aqueous solution **508** separates from the diene product **507**. The product diene **509** may be removed, and the aqueous solution **508** can be passed through a filter and/or one or more other unit operations **510** to remove traces of organic acids or other unwanted byproducts that can be produced during the dehydration reaction, thereby producing a purified water stream **502**. Optionally, the water stream **502** may be added to the alkenol or diol feed in **501**. For those skilled in the art, this process is commonly denoted as an "adiabatic reactor" and, in some embodiments, provides the most economical and energy efficient means of dehydrating a bio-alkenol. In calculating a WHSV, the weight of alcohol feed per hour is divided by the weight of catalyst contained in both reactors. Thus in the system described above with two reactors, each separate reactor will appear to have a WHSV equaling twice that of the overall process WHSV (feed to process/total catalyst, where total catalyst is reactor 1 + reactor 2; assuming, for the explanatory case described here, that each of reactor 1 and reactor 2 is charged with the same amount of catalyst).

[146] In some embodiments of the methods disclosed herein, a device for separation of the diene product from water (e.g., an aqueous solution that contains water and other components, for example, trace organic acids and/or other byproducts) is provided. For example, water may be separated from the diene product stream by fractionation through a distillation column. In some embodiments distillation may include injecting nitrogen, steam, or other volatile inert (*e.g.*, steam-stripping of the product stream as part of the separation process). In some embodiments where the product stream includes 1,3-butadiene, the diene is recovered using methods that include steam- or nitrogen-stripping of the product stream. Alternatively, physical separation of layers can be used under conditions where the diene is a liquid, for example, when the diene product contains a sufficiently high boiling point, for example, boiling at a temperature above about 30°C. In this case, separation may optionally be achieved with a decanter (**405/407** or **507/508**, as shown schematically in FIG 4 or FIG 5, respectively). The diene product will typically be the top layer formed upon condensation and is typically siphoned from the top of the decanter vessel with the separated aqueous layer (*i.e.*, typically bottom layer) drained (*e.g.*, continuously drained) from the bottom layer (*e.g.*, **407**, **508**). The separated aqueous layer (e.g., **407**, **508**) can optionally be filtered to remove impurities and the water recycled for addition to the alkenol or diol feed. Alternatively, the diene may be recovered by liquid-

liquid extraction techniques known in the art. In some embodiments where the product stream includes 1,3-butadiene, the diene is recovered using methods that include liquid-liquid extraction.

[147] In some embodiments, the alkenol or diol/input steam is introduced to the catalyst reactor (*e.g.*, **503** or **403**) at about 1 psig to about 200 psig, about 5 psig to about 150 psig, or about 15 psig to about 100 psig. In certain embodiments, the exit pressure from the catalyst reactor(s) can be controlled by at least one back pressure regulator located on the exit side of the reactor. An increase in pressure can be useful although in some embodiments, this does not lead to an increase in the rate of dehydration (*e.g.*, an increase in WHSV at a given temperature).

[148] Although not wishing to be bound by theory, it is well known that under certain conditions, crotyl alcohol may undergo isomerization to form 3-buten-2-ol [*see, e.g.*, U.S. Patent No. 2,373,956]. In catalytic dehydration of crotyl alcohol, isomerization of crotyl alcohol may be concurrent with dehydration. Under conditions of contact with the dehydration catalyst, isomerization of crotyl alcohol to 3-buten-2-ol may occur, in which case some of the diene product will be a result of the direct dehydration of 3-buten-2-ol, in the case that the dehydration catalyst is competent for 3-buten-2-ol dehydration to diene(s). These reaction pathways are shown schematically in FIG 6.

[149] In some embodiments a diene product produced as described herein can be utilized to make a drop-in diesel or jet fuel (*e.g.*, biofuel) or a lubricant (*e.g.*, biolubricant) in an energy-efficient manner. The term "drop-in" is used to indicate the new fuel prepared from the diene product can be used in commercial or military applications without the need for equipment changes or modifications. For example, the new fuels can meet the requirements of ASTM D1655 (via ASTM D7566), the standard for turbine fuels. Thus, the new fuels can be fully compatible with existing petroleum fuel standards, be used in commercial aircraft, and therefore be considered "drop-in fuels."

[150] In one embodiment, the methods taught herein may be utilized for conversion of an alkenol (*e.g.*, crotyl alcohol) or a diol that is produced biologically, for example, in a microbial fermentation process (*e.g.*, bio-crotyl alcohol), containing small to large amounts of water, for example, water from the fermentation broth and optionally additional added water, to a diene (*e.g.*, 1,3-butadiene) with high selectivity and chemical conversion. The 1,3-butadiene in turn is useful in preparing products that are environmentally beneficial and reduce greenhouse gases compared to petroleum equivalents by virtue of the biological

production of the alcohol and an energy efficient process of making the downstream products.

[151] An example of a method for making 6-carbon monomers from a four-carbon alkenol or diol as the starting material is shown schematically in FIG 7. The alkenol or diol feed **700** is added to the vaporization/mixing vessel **701** to which water feed **702** is added at some preselected amount. The output of **701** is transferred to the catalyst vessel **703** which contains the dehydration catalyst (*e.g.*, **206** or **304**, prepared as described above). The output from **703** is fed to a cooling/condenser system (**704**). The output from **704** is transferred to a decanter where an aqueous solution **707** separates from the diene or bio-diene product **705.** The aqueous solution **707** can be passed through a filter **708** and/or one or more unit operations to remove traces of organic acids or other unwanted byproducts that can be produced during the dehydration reaction, thereby producing a purified water stream **702**. Optionally, the water stream **702** may be added to the alcohol feed in **701**. The diene product **705** is fed to a dryer (**709**) (*e.g.*, a vessel charged with a dessicant medium, such as molecular sieves or similar inorganic drying agent) and subsequently undergoes a catalyzed double hydrocyanation to afford a product stream of adipoylnitrile (**710**). The product in **710** is fed to a hydrolysis reactor (**712**) to afford adipic acid (**713**) or reduced with hydrogen using a catalyst in reactor (**713**) to afford the products hexamethylene diamine (**714**).

[152] In embodiments of the dehydration methods disclosed herein in which the alkenol or diol is produced biologically (*e.g.*, bio-1-alkenol or bio-diol), contaminants (*e.g.*, organic contaminants) may be present in the alcohol-water mixture (*e.g.*, from fermentation broth), including but not limited to, esters, aldehydes, and/or ketones. Such contaminants can be tolerated in the dehydration reactions disclosed herein at various levels depending upon the alkenol (*e.g.*, bio-alkenol) or diol (*e.g.*, bio-diol) feedstock used. In some embodiments, up to about 0.5 wt-%, or up to about 5 wt-% contaminants (*e.g.*, organic contaminants) may be tolerated, for example, when crotyl alcohol (e.g., bio-crotyl alcohol) is the starting material.

[153] In some embodiments of the methods disclosed herein, removal of final traces of water and oxygenated organics (*e.g.*, ethers, aldehydes, and/or aldol-type products) from the diene (*e.g.*, bio-diene) product can be accomplished by passing the diene stream through a fixed bed of separation media, for example, activated alumina, molecular sieves, Celite, activated charcoal, size-exclusion type of media (*e.g.*, selective gas permeation membranes), or a combination thereof. For example, the media may be contained in a vessel shown schematically in FIG 7 as dryer **709**. In some embodiments, reactivation of the fixed-bed materials may be possible by heating under a purge of hydrocarbon or inert gas while

heating to temperature of about 50° to about 200° C, or about 100° C. In one embodiment, a series of membranes and/or bed of ionic-liquids that are well known for permitting selective passage of non-polar molecules and retaining more polar organics (*e.g.*, ethers and alcohols) can be used to dewater the diene product.

Biological production of alkenols and diols

[154] In some embodiments, alkenols and/or diols may be produced via microbial fermentation. The alkenol and/or diol products may be catalytically converted to diene products as described herein. In some embodiments, alkenol and/or diol products may be at least partially separated from the fermentation medium and dehydrated to produce diene products using catalyst compositions as described herein.

[155] In some embodiments, a microorganism that is used for production of alkenol(s) and/or diol(s) has been modified to produce a greater amount of the alkenol(s)and/or diol(s) than the parent microorganism from which it is derived. In other embodiments, a microorganism is used that produces the alkenol(s) and/or diol(s) via existing (*e.g.*, native) enzyme(s) and/or biosynthetic pathways. In some embodiments, the microorganism is a *Clostridium* strain.

[156] In some embodiments, microbial production of crotyl alcohol is achieved through the ability of the native promiscuous alcohol dehydrogenase (adhE, adhe2) in a microorganism, *e.g.*, a *Clostridium* strain, to convert crotonyl-CoA to crotonaldehyde. In some embodiments, microbial production of crotyl alcohol is achieved through the ability of the native promiscuous alcohol dehydrogenases (adhE, adhE2, bdhAB) to convert the crotonaldehyde to crotyl alcohol.

[157] In some embodiments, microbial production of crotyl alcohol is achieved through the deletion or inactivation of the butyryl-CoA dehydrogenase (bcd) and/or crotonyl-CoA reductase gene, or similar genes that are a part of butanoate/butanol, fatty acid, and amino acid degradation pathways in a microorganism., *e.g.*, a *Clostridium* organism.

[158] In some embodiments, the production of crotyl alcohol from an engineered microorganism, *e.g.* a *Clostridium* microorganism, is enhanced through treatment of the engineered *Clostridium* (*e.g.*, engineered to delete or inactivate the bcd gene) with one or more chemical mutagen(s), followed by selection under that bias the selection towards strains with increased crotyl alcohol production, selection in the presence of crotyl alcohol.

[159] In some embodiments, the production of crotyl alcohol from a non-engineered or non-modified microorganism, *e.g.*, a *Clostridium* microorganism, is enhanced by treatment

with one or more chemical mutagen(s), followed by selection under conditions that bias the selection towards strains with increased crotyl alcohol production, for example, but not limited to, selection in the presence of crotyl alcohol and/or another related alcohol, *e.g.*, propanol, pentenol, pentanol.

[160] A strategy is described herein whereby a microorganism, *e.g.*, a *Clostridium* microorganism, that produces *n*-butanol is converted into a microorganism that produces crotyl alcohol, for example, by deletion, inhibition, and/or inactivation of the activity of one or more enzyme(s) (*e.g.*, bcd, phosphotransbutyrylase (ptb), butyrate kinase (bk), CoT (CoA transferase), acetoacetate decarboxylase (aad)). In some embodiments, deletion, inhibition, and/or inactivation of CoT and/or aad reduces or eliminates production of acetone in an ABE producing microorganism, *e.g.*, a *Clostridium* microorganism, which improves crotyl alcohol yield. Other strategies include converting a microorganism, e.g., a *Clostridium* microorganism, into a microorganism that produces crotyl alcohol by overexpression of one or more enzyme(s) (*e.g.*, an enzyme of a glycolytic or pentose phosphate pathway that converts glucose and/or xylose to acetyl-CoA, a thiolase enzyme that converts acetyl-CoA to acaetoacetyl-CoA, a 3-hydroxy butyryl CoA dehydrogenase enzyme that converts acetoacetyl-CoA to 3-hydroxybutyryl-CoA, a crotonase enzyme that converts 3-hydroxybutyryl-CoA to crotonyl-CoA, an aldehyde dehydrogenase enzyme that converts crotonyl-CoA to crotonaldehyde, an alcohol dehydrogenase enzyme that converts crotonaldehyde to crotyl alcohol). In some embodiments, at least one enzyme of a butanol/butanoate pathway (*e.g.,* bcd) is deleted, inhibited, or inactivated, and at least one enzyme of a crotyl alcohol pathway (*e.g.*, an alcohol dehydrogenase enzyme) is overexpressed.

[161] Other strategies are described herein in which non-engineered microorganisms (e.g., microorganisms that produce *n*-butanol) may produce crotyl alcohol by adjustment of culture conditions to favor production of this product. For example, one or more substance(s), including but not limited to, one or more divalent metal ion(s) (e.g., Ca^{2+}, Co^{2+}, Zn^{2+}, and/or Mn^{2+}), iodoacetamide, myristoyl-CoA, N-ethylmaleimide, and/or palmitoyl-CoA may be included in the growth medium, thereby increasing production of crotyl alcohol versus a growth medium that does not include the substance(s). Such substance(s) may serve as inhibitors of one or more enzyme(s), including but not limited to, bcd, thereby increasing production of crotyl alcohol by the microorganism. In some embodiments, an SiHybrid may downregulate the activity of one or more enzyme(s), such as bcd.

[162] Methods are provided for producing one or more alkenol(s) or diol(s) in a microbial fermentation. The methods include culturing a microorganism that produces the alkenol(s) and/or diol(s) of interest (*e.g.*, crotyl alcohol) in a medium that contains a carbon source, such as, but not limited to, soluble sugar molecules produced from biomass (*e.g.*, in an acid and/or enzymatic hydrolysate of biomass) to support microbial growth for production of the alkenol(s) and/or diol(s).

[163] The methods for production of alkenol(s) and/or diol(s) (*e.g.*, crotyl alcohol) herein include fermentation with an engineered, mutagenized, or non-engineered, non-mutagenized microorganism (*e.g.*, *Clostridium* microorganism) as described herein in a bioreactor in a growth medium that contains a carbon source, such as, but not limited to, a liquid sugar-containing extract from biomass, such as a hydrolysate or conditioned hydrolysate (*e.g.*, conditioned to remove at least a portion of one or more inhibitor(s) of microbial growth and/or bioproduct (*e.g.*, alkenol and/or diol) production), prepared from biomass (*e.g.*, lignocellulosic biomass). In some embodiments, a liquid sugar containing extract such as cane juice and/or molasses is included in the growth medium.

[164] In some embodiments, the bioproduct production includes fermentation with a microorganism as described herein in an immobilized cell bioreactor (*i.e.*, a bioreactor containing cells that are immobilized on a support, *e.g.*, a solid support). In some embodiments, an immobilized cell bioreactor provides higher productivity due to the accumulation of increased productive cell mass within the bioreactor compared with a stirred tank (suspended cell) bioreactor. In some embodiments, the microbial cells form a biofilm on the support and/or between support particles in the growth medium.

[165] In other embodiments, for example but not limited to, embodiments in which a hydrolysate composition containing both liquid hydrolysate and solid residues is used, microorganisms may be grown in a non-immobilized system, such as an agitated fermentation reactor, *e.g.*, designed to provide adequate conditions for fermentation, including but not limited to mixing of components, gas removal, temperature control, and/or the ability to add and/or remove material from the reactor. Several fermentation operational moieties exist, including but not limited to batch, fed-batch, and continuous in single or multiple reactor configurations. Exemplar reactor types include but are not limited to agitated tanks, *e.g.*, where agitation is effected by a mechanical impeller, the addition and withdrawal of material, the addition of gas, and/or the recirculation of fermentation gas; corn and/or cane ethanol fermentation tanks; pharmaceutical fermentation vessels; vacuum fermentation systems; air-lift type reactors; fluidized bed reactors; anaerobic digestors; and

activated sludge reactors. In some embodiments, an extractive fermentation process is used (*e.g.*, gas stripping, liquid extraction, vacuum fermentation, extraction by absorption and/or adsorption by a solid material such as a polymeric material).

[166] In some embodiments, the alkenol and/or diol (*e.g.*, crotyl alcohol) production process herein includes continuous fermentation of a microorganism (continuous addition of conditioned hydrolyzed feedstock and withdrawal of product stream). Continuous fermentation minimizes the unproductive portions of the fermentation cycle, such as lag, growth, and turnaround time, thereby reducing capital cost, and reduces the number of inoculation events, thus minimizing operational costs and risk associated with human and process error.

[167] Fermentation may be aerobic or anaerobic, depending on the requirements of the bioproduct-producing microorganism.

[168] As known in the art, in addition to an appropriate carbon source, fermentation media must contain suitable nitrogen source(s), mineral salts, cofactors, buffers, and other components suitable for the growth of the cultures and promotion of the enzymatic pathway necessary for the production of the desired bioproduct. In some embodiments, salts and/or vitamin B12 or precursors thereof are included in the fermentation media. In some cases, hydrolyzed biomass may contain some or all of the nutrients required for growth, minimizing or obviating the need for additional supplemental material.

[169] One or more microorganism that is capable of producing one or more alkenol(s) or diol(s) of interest (*e.g.*, crotyl alcohol) may used in the fermentation methods described herein. In embodiments in which two or more microorganisms are used, the microorganisms may be the same or different microbial species and/or different strains of the same species.

[170] In some embodiments, the microorganisms are bacteria or fungi. In some embodiments, the microorganisms are a single species. In some embodiments, the microorganisms are a mixed culture of strains from the same species. In some embodiments, the microorganisms are a mixed culture of different species. In some embodiments, the microorganisms are an environmental isolate or strain derived therefrom.

[171] The following examples are intended to illustrate, but not limit, the invention.

EXAMPLES

Example 1

Testing the effect of crotyl alcohol on *Clostridium* *n*-butanol fermentations

[172] The effect of crotyl alcohol in the growth medium of a *Clostridium* fermentation was investigated. Production of *n*-butanol by a butanol-producing *Clostridium* strain was determined at various concentrations of crotyl alcohol in the fermentation medium. Seed culture and growth media were J2 for JR22. J2 media: A liquid yeast based media containing 6% glucose as a carbohydrate source. Crotyl alcohol was added to the J2 media to the following final concentrations: 0, 0.1, 1,2,4,6, and 8g/L. Crotyl alcohol concentration in the culture media was confirmed by submitting samples for HPLC analysis prior to inoculation. All cultures were inoculated at 10% volume from a seed cultured in J2 with 0 g/L crotyl alcohol. Culture volumes were 4 mL, grown in 10 mL conical tubes. Media and culture vials were deoxygenated prior to growth in an anaerobic chamber. Typically small scale cultures are grown in 15 mL conical tubes, where there are screw thread caps in place to reduce butanol evaporation but pressure from gas generated during the fermentation can be released. Conical tubes were used to reduce the possibility of evaporation of the crotyl alcohol during the fermentation. Time points were taken at 24 and 48 h, a single time point per vial. At each time point the absorbance at 600 nm was measured and a sample was submitted for HPLC analysis. Results for crotyl alcohol addition are shown as a percent of the control (no crotyl alcohol addition) in Fig. 15.

[173] Butanol tolerance of JR22 was investigated, for comparison with crotyl alcohol tolerance. The seed culture and growth media used were molasses media. (Molasses media: A liquid yeast based media containing 6% molasses as a carbohydrate source). Butanol was added to the molasses media to the following final concentrations: 0, 3, 4.5, 6.5, 8, 10, 12, 13, and 15 g/L. Butanol concentration in the culture media was confirmed by submitting samples for HPLC analysis prior to inoculation. All cultures were inoculated at 10% volume from a seed cultured in molasses media with 0 g/L butanol added to the media. Cultures volumes, growth conditions and sampling were performed as described for the crotyl alcohol samples above. Results for *n*-butanol addition are shown in Fig. 16.

[174] Data showing total solvent production (butanol, acetone, and ethanol) as a function of added crotyl alcohol are shown in Fig. 17.

[175] Data showing the uptake of crotyl alcohol, accounting for the increased total solvent production above the maximum theoretical based on sugar uptake, are shown in Table 1.

TABLE 1

Crotyl alcohol added (g/L)	Crotyl alcohol consumed (g/L)
0	0
1	0.7
2	1.5
4	3.1
6	4.0
8	2.0

[176] The data above demonstrate that the enzymatic steps are indeed non-selective for the substrate. These data provide direct evidence the enzymatic steps (adhE and adh2) are promiscuous in nature.

Example 2

Testing the effect of crotonic acid on *Clostridium* *n*-butanol fermentations

[177] The effect of crotyl alcohol in the growth medium of a *Clostridium* fermentation was investigated. Production of *n*-butanol by *Clostridium* was determined at various concentrations of crotyl alcohol in the fermentation medium. Seed culture and growth media were J2 for JR22. J2 media: A liquid yeast based media containing 6% glucose as a carbohydrate source. Crotonic acid was added to the J2 media to the following final concentrations: 0, 3, 6 g/L. Crotonic acid concentration in the culture media was confirmed by submitting samples for HPLC analysis prior to inoculation (data shown in tables below for crotonic acid added indicates the actual amount present as measured by HPLC). All cultures were inoculated at 20% volume from a seed cultured in J2 (strain JR22) with 0 g/L crotonic acid. Culture volumes were 100 mL, grown in 250 mL shake flasks. Shake flasks were deoxygenated prior to growth in an anaerobic chamber. Typically small scale cultures are grown in 250 mL shake flasks where there are screw thread and pressure releasing valves. At each time point the pH and absorbance at 600 nm was measured and a sample was submitted for HPLC analysis.

[178] Results for crotonic acid addition demonstrates Glucose uptake over time are shown in Fig. 18. Data showing the consumption of crotonic acid as a function of time are shown in Fig. 19. Plots showing the n-butanol titer as a function of crotonic acid added are shown in Fig. 20.

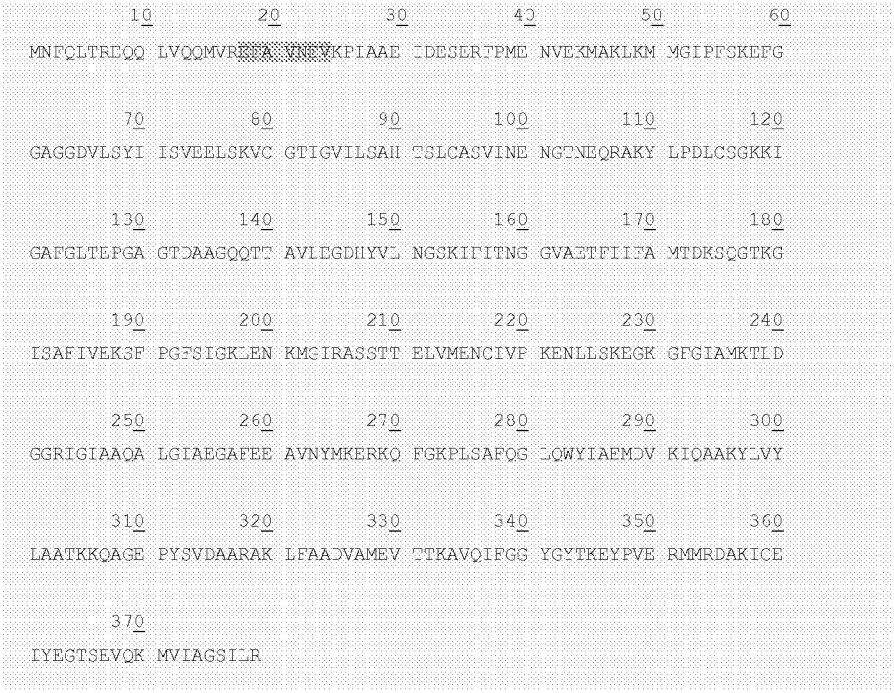
Example 3

Downregulation of the bcd gene by siHybrids in *Clostridium* for the production of crotyl alcohol from lignocellulosic hydrolysate or other fermentable feedstock with subsequent conversion of crotyl alcohol to butadiene via a dehydration catalyst

[179] This example demonstrates the engineering of a *Clostridium* strain that has the native genes shown in Fig. 21. The butanol production pathway in *Clostridium acetobutylicum* includes Ack, acetate kinase; Pta, phosphotransacetylase; AdhE, aldehyde/alcohol dehydrogenase; Thl, thiolase; Hbd, 3-hydroxybutyryl-CoA dehydrogenase; Crt, crotonase; Bcd, butyryl-CoA dehydrogenase; Ptb, phosphotransbutyrylase; Buk, butyrate kinase; CtfA/B, CoA transferase; Adc, acetoacetate decarboxylase; NADH, nicotinamide adenine dinucleotide (reduced form). The single reactions do not represent stoichiometric fermentation balances. (Scheme from Mazzoli (2012) www.ncbi.nlm.nih.gov/pmc/articles/PMC3962139/).

[180] A bcd siHybrid is designed to downregulate butyryl-CoA dehydrogenase without the need for time consuming plasmid production and transformation. With the bcd (butyryl-CoA dehydrogenase) gene silenced utilizing siHybrids to downregulate the bcd gene, the native promiscuous alcohol dehydrogenase (adhE, adhe2) can convert crotonyl-CoA to crotonaldehyde. In addition, the native promiscuous alcohol dehydrogenases (adhE, adhE2, bdhAB) can also convert the crotonaldehyde to crotyl alcohol as shown in Fig. 22. The Crotyl Alcohol Production Pathway in an engineered *Clostridium* species with inactivation of the bcd gene includes Ack, acetate kinase; Pta, phosphotransacetylase; AdhE, AdhE2, aldehyde/alcohol dehydrogenase; BdhA, BdhB, butanol dehydrogenase; Thl, thiolase; Hbd, 3-hydroxybutyryl-CoA dehydrogenase; Crt, crotonase; Bcd, butyryl-CoA dehydrogenase; Ptb, phosphotransbutyrylase; Buk, butyrate kinase; CtfA/B, CoA transferase; Adc, acetoacetate decarboxylase; NADH, nicotinamide adenine dinucleotide (reduced form). The single reactions do not represent stoichiometric fermentation balances.

First, a siHybrid is constructed using a random twenty-one base pair sequence from the published bcd gene sequence of *C. beijerinckii* (NCIMB 8052). The amino acid sequence of the bcd gene, Cbei_0322, is depicted in SEQ ID NO:1. The siHybrid is constructed with a random 7 amino acid length segment from this sequence. The region chosen for SiHybrid construction is highlighted.



(SEQ ID NO:1)

[181] Region sense and antisense strands are constructed with two nucleotide 3' uridine over hangs (GenScript, Piscataway, NJ). The region from amino acids 18-24 of the bcd gene, Cbei_0322 was chosen for its DNA homology to C. beijerinckii strain NRRL B593 and *C. saccharobutylicum* DSM 13864. The sequence was queried for homology with other unrelated genes using the BLAST (basic local alignment search tool) bioinformatics tool. The closest additional sequence shares only 14 of the 21 base pairs from amino acid region 18-24. Therefore, the siHybrid should not interfere with the translation of any additional genes. The sense strand is composed of RNA of the sequence 5' CUU CAU UUA CUG CGA AUU CUC UU 3'. (SEQ ID NO:2) The antisense strand is composed of DNA of the sequence 5' GAG AAT TCG CAG TAA ATG AAG TT 3'. (SEQ ID NO:3). Sense and antisense strands are annealed together in equimolar amounts in the presence of 10 mM Tris-HCl (pH 8.0) by denaturing for 5 minutes at 94° C and then reannealed at 53° C for 3 hours. Annealed strands are then slowly cooled to room temperature. This siHybrid is added to the fermentation medium at a concentration of 4 μg/ml.

[182] A culture of C. beijerinckii is started overnight from glycerol stock in minimal medium absent of bcd siHybrid strands. When cultures reach an optical density at 600nm of 1.0, a 10% inoculation is performed into a fermentataion medium (e.g., lignocellulosic hydrolysate), for example, with defined added nutrients under anaerobic conditions in a

bioreactor containing either 4 μg/ml of the bcd siHybrid, or medium absent of siHybrid. Cultures are incubated anaerobically, shaking at 100 rpm, at 32 C for 48 hours, with time points taken at 24, 48, and 72 hours. Fermenation broth is filtered and analyzed by HPLC for butanol, butyric acid, crotyl alcohol, and crotonic acid. If bcd activity is downregulated, HPLC results from siHybrid-containing medium will show higher amounts of crotyl alcohol and crotonic acid, while producing less butanol and butyric acid than the control. Fermenation broth is also analyzed for protein suppression (e.g., Bcd protein expression levels) by Western blot.HPLC is used to monitor the crotyl alcohol production during fermentation. Western blot analysis is also performed to evaluate the Bcd protein expression levels.

[183] At the end of fermentation, crotyl alcohol may be collected from the fermentation broth and is converted with a dehydration catalyst to bio-1,3-butadiene as described herein.

[184] The DNA sequence of Cbei_0322 from NCIMB 8052 is depicted in SEQ ID NO:4. The region chosen for SiHybrid construction is highlighted.

atgaatttccaattaactagagaacaacaattagtacaacaaatggttagagaattcgcagtaaatgaagttaagccaatagctgctga
aatcgacgaatcagaaagattccctatggaaaacgttgaaaaaatggctaagcttaaaatgatgggtatcccattttctaaagaatttgg
tggagcaggcggagatgttctttcatatataatatctgtggaagaattatcaaaagtttgtggtactacaggagttattctttcagcgcata
catcattatgtgcatcagtaattaatgaaaatggaactaacgaacaaagagcaaaatatttgccagatctttgtagtggtaagaaaatcg
gtgctttcggattaacagaaccaggcgctggtacagatgctgcaggacaacaaacaactgctgtattagaaggagaccattatgtatt
aaatggttcaaaaatcttcataacaaatggtggagttgctgaaactttcataatatttgctatgacagataagagtcaaggaacaaaagg
aatttctgcattcatagtagaaaagtcattcccaggattctcaataggaaaattagaaaacaagatggggatcagagcatcttcaacta
ctgagttagttatggaaaactgtatagtaccaaaagaaaacctacttagcaaagaaggtaagggatttggtatagcaatgaaaactctt
gatggaggaagaattggtatagctgctcaagctttaggtattgcagaaggagcttttgaagaagctgttaactatatgaaagaaagaa
aacaatttggtaaaccattatcagcattccaaggattacaatggtatatagctgaaatggatgttaaaatccaagctgctaaatacttagt
atacctagctgcaacaaagaagcaagctggtgagccttactcagtggatgctgcaagagctaaattatttgcggcagatgttgcaatg
gaagttacaactaaagcagttcaaatctttggtggatatggttacactaaggaataccagtagaaagaatgatgagagatgctaaaata
tgcgaaatctacgaaggaacttcagaagttcaaaagatggttatcgcaggaagcattttaagatag (SEQ ID NO:4)

[185] The DNA sequence of the bcd gene *from C. beijerinckii* strain NRRL B593 is depicted in SEQ ID NO:5. The region chosen for siHybrid construction is highlighted,

atgaatttccaattaactagagaacaacaattagtacaacaaatggttagagaattcgcagtaaatgaagttaagccaat
agctgctgaaatcgacgaaacagaaagattccctatggaaaacgttgaaaaaatggctaagcttaaaatgatgggtatc
ccattttctaaagaatttggtggagcaggcggagatgttctttcatatataatagctgtggaagaattatcaaaagtttgtg
gtactacaggagttattctttcagcgcatacatcattatgtgcatcagtaattaatgaaaatggaactaacgaacaaagag
caaaatatttacctgatctttgcagcggtaaaaagatcggtgctttcggattaactgaaccaggtgctggtacagatgctgc
aggacaacaaacaactgctgtattagaaggggatcattatgtattaaatggttcaaaaatcttcataacaaatggtggagt
tgctgaaactttcataatatttgctatgacagataagagtcaaggaacaaaagaatttctgcattcatagtagaaaagtca
ttcccaggattctcaataggaaaattagaaaataagatggggatcagagcatcttcaactactgagttagttatggaaaac
tgcatagtaccaaaagaaaacctacttagcaaagaaggtaagggatttggtatagcaatgaaaactcttgatggaggaa
gaattggtatagctgctcaagctttaggtattgcagaaggagcttttgaagaagctgttaactatatgaaagaaagaaaac
aatttggtaaaccattatcagcattccaaggattacaatggtatatagctgaaatggatgttaaaatccaagctgctaaata
cttagtatacctagctgcaacaaagaagcaagctggtgagccttactcagtagatgctgcaagagctaaattatttgctgc
agatgttgcaatggaagttacaactaaagcagttcaaatctttggtggatatggttacactaaagaatacccagtagaaag
aatgatgagagatgctaaaatatgcgaaatctacgaaggaacttcagaagttcaaaagatggttatcgcaggaagcattt
taagata

(SEQ ID NO:5)

[186] The DNA sequence of the bcd gene from *C. saccharobutylicum* DSM 13864 is depticted in SEQ ID NO:6. The region chosen for siHybrid construction is highlighted.

atgaattttaagttaactagagaacaagaattaatacaacaaatggttagagaattcgcagtaaatgaagttaaaccaat
agctgctgaaatcgatgagacagaacaatttccgatggaaaatgttaaaaaaatggctgaattaggaatgatgggtattc
cattttctaaagaagtaggaggagcaggcggagatgttctttcttatataatagctgtagaagaattatcaaaagtgtgtg
gtactacaggtgttatactttcagcacatacatcattatgtgcatcagtaattaacgaaaatggtactccagctcaaaaaga
aaaatatttagcagatctttgtagtggtaagaaaattggtgctttggtttaactgaaccaggtgctggtacagatgctgctg
gacaacaaacaacagcaacattagaaggagatcattatgtattaaatgggtcaaaaatattcataacaaatggtggagtt
gctgaaactttcataatttttgctatgacagataagagccaaggaactagaggaatttctgcatttgtagtagaaaaatcat
tccctggattctcagtaggaaaattagaaaacaagatgggtattagagcatcttcaactactgaattagttatggaaaact
gtatagtaccaaaagaaaacttacttggtaaagaaggtaagggatttggtatagcaatgaagactcttgatggaggaag
aattggtatagctgctcaagctttaggtattgcagaaggagcttttgaagaagcagttgcatacatgaaagaaagaaaac
aatttaataaaccactttcagcattccaaggattacaatggtatattgctgaaatggacgttaagatagacgctgctaagc
atttagtatataaagcagcatgcaagaaacaagcgggtcaaccttattcagttgatgcggctagagctaagttgtttgcag
cagacgttgcaatggaagttacaactaaggcagtacaaatctttggtggatatggttacactaaggaatacccagtagaa
agaatgatgagagatgctaagataactgaaatctatgaaggaacttcagaagttcaaaagatggttattgcaggaagcat
tttaagatagg

(SEQ ID NO:6)

Example 4

Engineered *Clostridium* via bcd inactivation for the production of crotyl alcohol from lignocellulosic hydrolysate or other fermentable feedstock with subsequent conversion of crotyl alcohol to butadiene via a dehydration catalyst

[187] Example 3 describes the engineering of a *Clostridium* strain that has the native genes with the bcd (butyryl-CoA dehydrogenase) gene inactivated via an intron. The native promiscuous alcohol dehydrogenase (adhE, adhe2) can convert crotonyl-CoA to

crotonaldehyde. In addition, the native promiscuous alcohol dehydrogenases (adhE, adhE2, bdhAB) can also convert the crotonaldehyde to crotyl alcohol.

[188] Preliminary inactivation of bcd is done using targetron, a gene knockout system with proven efficacy in *Clostridium* species (available from Sigma Aldrich). The targetron system works by inserting a group II intron via the activity of an RNA-protein complex into the gene of interest. Primers are generated for specific targeting of the group II intron into the bcd gene. The re-targeted intron is generated by PCR, and this segment of the group II intron is ligated into a linearized vector that contains the rest of the group II intron components, as well as an antibiotic resistance gene that is flanked by Flp recombinase recognition sites. The vector is transformed by methods known in the art into the *Clostridium* host and the RNA-protein complex is expressed. This RNA-protein complex locates the genomic target, inserts RNA and reverse transcribes cDNA. Host enzymes repair and create a permanent insertion into the bcd gene of the group II intron. Chromosomal insertion mutants are selected with the antibiotic marker. The antibiotic resistance marker is removed by transformation with a vector that expresses Flp, excising the antibiotic resistance marker. Verification of disruption of the bcd gene is performed by colony PCR using gene and intron specific primers.

[189] Gene disruption using targetron is performed with pJIR750ai containing a group II intron that has been retargeted to the bcd gene in *Clostridium beijerinckii*, as shown in Fig. 23. The intron is expressed from a beta-2-p promoter. This intron contains a Kanamycin resistance (KanR) marker with its promoter (P1) inserted in the orientation opposite that of the intron transcription. This KanR marker is disrupted by a self-splicing td group I intron inserted in the forward orientation. During retrotransposition via an RNA intermediate, the td intron is spliced, activating the KanR marker, which is then selected after the intron has integrated into the DNA target site. Flp recombinase recognition (FRT) sites flank the KanR marker gene. Expression of the Flp protein from a separate plasmid leads to efficient excision of the KanR marker from the integrated targetron, enabling multiple sequential disruptions.

[190] The engineered *Clostridium* strain is cultivated from a glycerol stock and inoculated into a lignocellulosic hydrolysate or other growth medium with nutrients for growth of the microorganism under anaerobic conditions in a bioreactor. HPLC is used to monitor the crotyl alcohol production during fermentation. At the end of fermentation, crotyl alcohol in the fermentation broth, optionally separated from the fermentation broth, is converted to 1,3-butadiene with a dehydration catalyst as disclosed herein

Example 5

Inactivation of bcd gene by homologous recombination to insert a selectable marker or deletion of a portion of the bcd gene

[191] The bcd gene and approximately 1kb of flanking regions (sequence homology upstream and downstream) is cloned into a suicide vector. A selectable marker, such as erythromycin resistance, is used to replace all or a portion of the bcd gene while preserving the integrity of the operon with an in frame deletion. The plasmid is transformed into *Clostridium* by methods known in the art. Since the plasmid is unable to replicate in *Clostridium*, *Clostridium* with resistance to the selectable marker undergoes homologous recombination at the upstream, downstream, or at both upstream and downstream sequences. Selectable marker resistant transformants are screened by PCR to identify double recombinant events. The selectable marker maybe removed using strategies known in the art to create a markerless knockout.

[192] The resulting engineered strain has an inactivated bcd gene and is able to produce crotyl alcohol. The engineered *Clostridium* strain is cultivated from a glycerol stock and inoculated into a lignocellulosic hydrolysate or other growth medium with nutrients for growth of the microorganism under anaerobic conditions in a bioreactor. HPLC can be used to monitor the crotyl alcohol production during fermentation. At the end of fermentation, crotyl alcohol in the fermentation broth, optionally separated from the fermentation broth, is converted to 1,3-butadiene with a dehydration catalyst as disclosed herein..

Example 6

Engineered and optimized *Clostridium* via bcd inactivation for production of crotyl alcohol, followed by directed evolution to optimize crotyl alcohol production from lignocellulosic hydrolysate or other fermentable feedstock with subsequent conversion of crotyl alcohol to butadiene via a dehydration catalyst

[193] Methods described in Example 4 will be followed to engineer *Clostridium* with an inactivated bcd gene. After inactivation of the bcd gene the production of crotyl alcohol will be optimized via directed evolution. The bcd knockout *Clostridium* is treated with mutagen (*e.g.*, both ethyl methanesulfonate (EMS) and N-methyl-N`-nitro-N-nitrosoguanidine (NTG) have proven efficacy for mutagenesis in *Clostridium*). Mutagenized bacteria are then grown in the presence of selection to bias the bacterial pool toward the desired outcome. Growth in the presence of crotyl alcohol is employed to select

organisms with increased tolerance to crotyl alcohol. Growth in the presence of lignocellulosic compounds typically found to be inhibitory may also be employed, to select for increased tolerance to these compounds found in hydrolysates containing lignin. Selections for increased productivity may also be employed.

[194] In addition or alternatively, metabolic flux analysis (MFA) is used for the determination of metabolic pathway fluxes in order to 1) verify that deletion of bcd leads to a significant accumulation of crotyl alcohol, 2) identify nodes that are potential bottlenecks to crotyl alcohol biosynthesis, and 3) identify competing biochemical pathways that direct carbon flow away from crotyl alcohol for further engineering. In this approach, the intracellular fluxes are calculated by using a stoichiometric model constructed from major pathway reactions and mass balances around intracellular metabolites. Intracellular fluxes are estimated based on measurable quantities, in particular, the rate of formation of extracellular metabolites. A set of measured extracellular fluxes including uptake rates of substrates and secretion rates of metabolites are used as inputs. The resulting flux calculation is a metabolic flux map showing biochemical reactions along with an estimate of the steady state rate at which each reaction occurs. This information is used to further engineer and optimize the strain for crotyl alcohol production.

[195] The resulting engineered *Clostridium* strain optimized for crotyl alcohol tolerance is cultivated from a glycerol stock and inoculated into a growth medium under anaerobic conditions in a bioreactor. HPLC can be used to monitor the crotyl alcohol production during fermentation. At the end of fermentation, crotyl alcohol in the fermentation broth, optionally separated from the fermentation broth, is converted to 1,3-butadiene with a dehydration catalyst as disclosed herein.

[196] The γ-alumina used for preparation of Catalysts **1** – **5** (Examples 7 – 10, 12, *infra*) was supplied by Strem Chemicals (min. 97%; surface area 210 m^2/g; product number 13-2525; lot number 23996900).

Example 7

[197] **Catalyst 1** was made by scaling the following method sufficient to prepare about 50g of finished catalyst: 1.5 wt-% of NaOH was loaded onto γ-alumina by incipient wetness impregnation. The NaOH solution contained 0.06 g of NaOH dissolved in water to make 4

mL of solution. The clear solution was added to 4 g of γ-alumina and mixed for about 5 min. The impregnated carrier was then dried at 200°C for 16 h to obtain the final catalyst.

Example 8

[198] Catalyst 2. γ-Alumina (60 g) was slurried in water (a portion, sufficient to create a slurry, taken from a total of 100 mL); $NaHSO_4$ (5 g) was dissolved in the remainder of the total of 100 mL of water to give a clear solution; the alumina slurry and $NaHSO_4$ solution were combined and stirred well; and the resulting mixture was taken to free-flowing dryness, by drying (ambient to about 200°C) overnight under a blanket of dry nitrogen with a slow nitrogen purge.

Example 9

[199] Catalyst 3 was made by loading 5.0g $Ca(H_2PO_4)_2{\cdot}H_2O$ onto 45g γ-alumina by incipient wetness impregnation. The impregnated carrier was then calcined at 300°C for 24 h to obtain the final catalyst.

Example 10

[200] Catalyst 4. γ-Alumina (49 g) was slurried in 40 mL of water; $Ca(H_2PO_4)_2{\cdot}H_2O$ (4.30 g, 17.1 mmol) and H_3PO_4 (0.5 mL of 85%, 0.425 g of H_3PO_4, 4.34 mmol) were dissolved in 50 mL of water to give a clear solution; the alumina slurry and $Ca(H_2PO_4)_2/H_3PO_4$ solution were combined and stirred well; and the resulting mixture was taken to free-flowing dryness, by drying (ambient to about 200°C) overnight under a blanket of dry nitrogen with a slow nitrogen purge.

Example 11

Catalytic performance in dehydration of crotyl alcohol to 1,3-butadiene.

[201] Catalyst examples **1-4** prepared above were tested in a fixed-bed test unit. In the test, a crotyl alcohol feed (either neat, or diluted as indicated in Table 2, below) was passed over a catalyst bed (42 – 54g) at 1 atm and a WHSV ([g crotyl alcohol]/[g catalyst]/hour) and bed temperature, as indicated in Table 2, below. The reaction products at the reactor outlet were trapped in serial traps, the first, initially empty, and maintained at 0 - 5°C, the second, initially toluene-filled, and maintained at -78°C, and then sampled and analyzed offline by gas chromatography with flame ionization detection.

TABLE 2. Crotyl Alcohol Dehydration Results.

	WHSV (h^{-1})	T (°C)	Diluent (wt%)	Crotyl Alcohol conversion	1,3-butadiene selectivity
Catalyst **1**	0.2	380	none	90%	<40%
Catalyst **2**	0.8	280	water (10)	99%	90%
Catalyst **3**	0.3	380	none	99%	<50%
Catalyst **4**	0.9	280	water (10)	99%	95

Example 12

[202] **Catalyst 5**. γ-Alumina (80 g) was slurried in 70 mL of water; $Ca(H_2PO_4)_2 \cdot H_2O$ (6.8 g, 27.0 mmol) was dissolved in 50 mL of water; H_3PO_4 (0.82 mL of 85%, 0.694 g of H_3PO_4, 7.09 mmol) was diluted in 10 mL of water; the $Ca(H_2PO_4)_2$ and H_3PO_4 solutions were combined to give a clear solution; the alumina slurry and $Ca(H_2PO_4)_2/H_3PO_4$ solution were combined and stirred well; and the resulting mixture was taken to free-flowing dryness, by drying (ambient to about 200°C) overnight under a blanket of dry nitrogen with a slow nitrogen purge. The resulting material was thoroughly wetted with ethanol (a portion, sufficient to wet the solid, taken from a total of 150 mL); diethoxydiphenylsilane (1 g) was dissolved in the remainder of the total of 150 mL of ethanol to give a clear solution; the ethanol-wet $Ca(H_2PO_4)_2/H_3PO_4$-treated alumina and diethoxydiphenylsilane solution were combined and stirred well; and the resulting mixture was taken to free-flowing dryness, by drying (ambient to about 200°C) overnight under a blanket of dry nitrogen with a slow nitrogen purge.

Example 13

[203] **Catalyst 6** is made by adding 3.3 wt-% of Ca^{+2} onto alumina by incipient wetness impregnation. The impregnation solution is prepared by dissolving $Ca(HSO_4)_2$ and $Ca(SO_4)$ in water. The solution contains 0.066 g of Ca^{+2} in 1.3 mL solution. The clear solution is added to 2 g of alumina and mixed for about 5 min. The impregnated carrier is then calcined at 200 °C for 6 h to obtain the final catalyst.

Example 14

[204] This invention **Catalyst 7** is made by adding 2 wt-% of Ca^{+2} onto γ-alumina (powder, surface area >250 m^2/g) by incipient wetness impregnation. The carrier is first

calcined at 600 °C for 2 h. The impregnation solution is prepared by dissolving $Ca(SO_4)$ (136 mg) in water along with $NaHSO_4$ (142 mg). The solution contains 0.04 g of Ca^{+2} and an equal molar concentration of hydrogen sulfate and sulfate ions in 1.3 mL solution. The clear solution is added to 2 g of alumina and mixed for about 5 min. The impregnated carrier is then calcined at about 250 to 550 °C for 6 h to obtain the final catalyst.

Example 15

[205] This invention **Catalyst 8** is made by adding 2 wt-% of Ca^{+2} onto γ-alumina (powder, surface area >250 m^2/g) by incipient wetness impregnation. The carrier is first calcined at 600 °C for 2 h. The impregnation solution is prepared by dissolving $Ca(HPO_4)$, $Ca(H_2PO_4)_2$, and phosphoric acid (H_3PO_4) in a molar ratio of 5:5:1 in water. The solution contains 0.04 g of Ca^{+2} cations in 1.3 mL solution. The clear solution is added to 2 g of alumina and mixed for about 5 min. The impregnated carrier is then calcined at about 250 to 550 °C for 6 h to obtain the final catalyst.

Example 16

[206] This invention **Catalyst 9** is made by adding 2 wt-% of Ca^{+2} onto γ-alumina extrudate (1/16" diameter) by incipient wetness impregnation. The carrier is first calcined at 600 °C for 2 h. The impregnation solution is prepared by dissolving $Ca(HPO_4)$, $Ca(H_2PO_4)_2$, and phosphoric acid (H_3PO_4) in a molar ratio of 5:5:1 in water. The solution contains 0.4 g of Ca^{+2} cations in 13 mL solution. The clear solution is added to 20 g of alumina and mixed for about 5 min. The impregnated carrier is then calcined at about 250 to 550 °C for 6 h to obtain the final catalyst.

Example 17

[207] This invention **Catalyst 10** is made by adding 2 wt-% of Ca^{+2} onto γ-alumina extrudate (1/8" diameter) by incipient wetness impregnation. The carrier is first calcined at 600 °C for 2 h. The impregnation solution is prepared by dissolving $Ca(SO_4)$ (1.36 g) in water along with $NaHSO_4$ (1.42 g). The solution contains 0.4 g of Ca^{+2} and an equal molar concentration of hydrogen sulfate and sulfate ions in 13 mL solution. The clear solution is added to 20 g of alumina extrudate and mixed for about 5 min. The impregnated carrier is then calcined at about 250 to 550 °C for 6 h to obtain the final catalyst.

Example 18

[208] This invention **Catalyst 11** is made by adding 2 wt-% of Ca^{+2} onto γ-alumina extrudate (1/8" diameter) by incipient wetness impregnation. The carrier is first calcined at 600 °C for 2 hr. The impregnation solution is prepared by dissolving $Ca(SO_4)$ (1.36 g) in water along with $NaHSO_4$ (1.42 g). The solution contains 0.4 g of Ca^{+2} and an equal molar concentration of hydrogen sulfate and sulfate ions in 13 mL solution. The clear solution is added to 20 g of alumina extrudate and mixed for about 5 min. The impregnated carrier is then calcined at about 250 to 550 °C for 6 h to obtain the final catalyst. This material is treated with an ethanol (15 mL) solution containing $Ph_2Si(OEt)_2$ (0.74 g) and mixed for 5 min and then placed under reduced pressure (400 torr) and heated to 50 °C for 2 hr and then heated to 200 °C for 4 hr.

Example 19

Conversion of crotonaldehyde to crotyl alcohol in Clostridium fermentation

Microorganism and culture medium

[209] ABE-producing *Clostridium saccharobutylicum* strains were used for the following experiments, including publicly available *Clostridium saccharobutylicum* P262, to demonstrate the fermentability of crotyl alcohol.

[210] J2 Media with 6% glucose was used to grow *Clostridium* cells for crotyl alcohol production. Pre-seed was inoculated with 0.4% (v/v) of cells from glycerol stock. The inoculum transfer from pre-seed to seed tank was made to achieve a final OD of 1 (equal to 0.32 g of dry cell weight per L of broth) in the seed tanks.

[211] For confirming the *adh* activity, the microbial cultures were spiked with different concentrations of crotonaldehyde during the solventogenesis stage. Spiking concentrations of crotonaldehyde ranged from 0 to 2 g/L. Since crotonaldehyde is very toxic to the microorganism, fed-batch fermentation was also done to test the tolerance of the microorganism. Small amount of crotonaldehyde were slowly added into fermentation to final concentration of 2 g/L over 6 hours. Samples were taken immediately and 24 hours after crotonaldehyde addition.

Alcohol Dehydrogenase Activity

[212] Fig. 24 shows the production of crotyl alcohol in the microbial cultures. The microorganism was able to take up crotonaldehyde and produce crotyl alcohol. The

reaction is relatively fast because crotonaldehyde is toxic to the microorganism, which is shown in Fig. 25 with no more butanol produced after the addition of crotonaldehyde at the concentration higher than 1 g/L.

[213] Fig. 26 shows crotyl alcohol production with different concentrations of crotonaldehyde addition.

[214] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

[215] While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

[216] Although the foregoing invention has been described in some detail by way of illustration and examples for purposes of clarity of understanding, it will be apparent to those skilled in the art that certain changes and modifications may be practiced without departing from the spirit and scope of the invention. Therefore, the description should not be construed as limiting the scope of the invention.

[217] All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entireties for all purposes and to the same extent as if each individual publication, patent, or patent application were specifically and individually indicated to be so incorporated by reference.

CLAIMS

We claim:

1. A method for dehydrating an alkenol or a diol to a diene, comprising:

contacting and heating said alkenol or diol with at least one catalyst that comprises an inorganic support, one or more promoter(s) selected from one or more Group 1 element(s), one or more Group 2 element(s), and combinations thereof, and one or more buffer-adjusted anion(s) at a WHSV at least about 0.3 hr^{-1},

thereby producing a diene product that comprises one or more diene(s) at a one-pass yield greater than about 73 mol%.

2. A method according to claim 1, wherein said WHSV is about 0.3 hr^{-1} to about 10 hr^{-1}.

3. A method according to claim 1, wherein said alkenol or diol is in a mixture with about 1 ppm to about 93 wt% water.

4. A method according to claim 1, wherein the selectivity of diene production is at least about 75%.

5. A method according to claim 1, wherein said alkenol is a bio-alkenol.

6. A method according to claim 1, wherein said alkenol is crotyl alcohol.

7. A method according to claim 1, wherein said alkenol is bio-crotyl alcohol.

8. A method according to claim 1, wherein said alkenol is a C_4 to C_6 alkenol

9. A method according to claim 1, wherein said one or more diene(s) is 1,3-butadiene.

10. A method according to claim 4, wherein the selectivity of diene production is greater than about 95%.

11. A method according to claim 4, wherein the selectivity of diene production is about 90% to about 99%.

12. A method according to claim 1, wherein one-pass conversion of said alkenol or diol is greater than about 95 mol%.

13. The method according to claim 3, wherein said mixture comprises about 15 to about 70 wt% water.

14. A method according to claim 1, wherein said inorganic support comprises γ-

alumina.

15. A method according to claim 1, wherein said catalyst is further modified by treatment with at least one organosilane.

16. A method according to claim 15, wherein said organosilane comprises an alkoxysilane.

17. A method according to claim 15, wherein said organosilane comprises a chlorosilane.

18. A method according to claim 1, further comprising providing at least one carrier gas.

19. A method according to claim 18, wherein said carrier gas comprises nitrogen and/or argon, and mixtures thereof.

20. A method according to claim 1, wherein said heating comprises a temperature of about 200° C to about 440° C.

21. The method according to claim 20, wherein said temperature comprises about 250° C to about 320° C.

22. A method according to claim 1, further comprising separating water from said diene product, thereby producing a dry diene product.

23. A method according to claim 9, comprising contacting said 1,3-butadiene product with a second catalyst under conditions sufficient to form 1-butene.

24. A method according to claim 23, wherein said 1-butene is contacted with a third catalyst selected from a Ziegler-Natta catalyst, a mesoporous oligomerization catalyst, and an acid catalyst under conditions sufficient to form oligomers.

25. A method according to claim 24, further comprising using said oligomers to produce a diesel fuel.

26. A method according to claim 25 wherein said diesel fuel comprises a flashpoint of about 38° C to about 100° C, a Cetane rating of about 45 to about 60, and aromatic content of less than about 0.5 wt-%.

27. A method according to claim 24, further comprising using said oligomers to produce a jet fuel.

28. A method according to claim 27, wherein said jet fuel comprises a flashpoint of

about 38° C to about 100° C, a cold flow viscosity of less than about 8.0 cSt at -20 °C, and aromatic content of less than about 0.5 wt-%.

29. A method according to claim 1, wherein the promoter is selected from Mg, Ca, Sr, Ba, and combinations thereof.

30. A method according to claim 29, wherein the promoter is Ca.

31. A method according to claim 1, wherein the buffer-adjusted anion is selected from SO_4^{-2}, $H_2PO_4^{-1}$, and mixtures thereof.

32. A method for dehydrating an alkenol or a diol to a diene, comprising:

contacting and heating said alkenol or diol with at least one catalyst that comprises a calcium-modified inorganic support and one or more buffer-adjusted anion(s),

thereby producing a diene product that comprises one or more diene(s) at a one-pass yield greater than about 80 mol%.

33. A method according to claim 32, wherein said alkenol is a bio-alkenol.

34. A method according to claim 32, wherein said alkenol is crotyl alcohol.

35. A method according to claim 32, wherein said alkenol is bio-crotyl alcohol.

36. A method according to claim 32, wherein the alkenol is a C_4 to C_6 alkenol

37. A method according to claim 32, wherein said diene product is 1,3-butadiene.

38. A method according to claim 32, wherein said alkenol is in a mixture with about 1 ppm to about 93 wt-% water.

39. A method according to claim 32, wherein the contacting is at a WHSV of about 0.3 hr^{-1} to about 10 hr^{-1}.

40. A method according to claim 32, wherein said catalyst is further modified by treatment with at least one organosilane.

41. A catalyst composition for producing dienes from alkenols or diols with high selectivity, comprising:

an inorganic support that is modified with at least one Group 1 element, at least one Group 2 element, or a combination thereof;

one or more buffer-adjusted anion;

and optionally, at least one organosilane.

42. A catalyst composition according to claim 41, comprising at least one Group 2 element selected from Mg, Ca, Sr, and Ba.

43. A catalyst composition according to claim 42, wherein the Group 2 element is Ca.

44. A catalyst composition according to claim 41, wherein the buffer-adjusted anion is selected from SO_4^{-2}, $H_2PO_4^{-1}$, and mixtures thereof.

45. A catalyst composition according to claim 41, wherein the buffer-adjusted anion is $H_2PO_4^{-1}$, wherein $H_2PO_4^{-1}$ is a component of a mixture that further optionally comprises one or more additional anions selected from HPO_4^{-2} and PO_4^{-3} and one or more charge balancing counter cations selected from H^{+1}, Li^{+1}, Na^{+1}, K^{+1}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, and combinations thereof.

46. A catalyst composition according to claim 41, comprising an organosilane, wherein the organosilane is diethoxydiphenylsilane.

47. A catalyst composition according to claim 41, wherein the inorganic support is γ-alumina or zinc aluminate.

48. A method of making a catalyst composition, comprising:

a) modifying an inorganic support with at least one Group 2 element and at least one buffer-adjusted anion to produce a first modified inorganic support, wherein the first modified inorganic support comprises said at least one Group 2 element and said at least one buffer-adjusted anion;

b) calcining the first modified inorganic support to produce a calcined first modified inorganic support;

c) contacting the calcined first modified inorganic support with at least one organosilane to produce a second modified inorganic support, wherein the second modified inorganic support comprises said at least one Group 2 element, said at least one buffer-adjusted anion, and said at least one organosilane, or fragment thereof; and

d) calcining the second modified inorganic support to produce the catalyst composition.

49. A method for dehydrating crotyl alcohol to a diene product, comprising:

contacting and heating said crotyl alcohol with at least one catalyst that

comprises an inorganic support, one or more promoter(s) selected from one or more Group 1 element(s), one or more Group 2 element(s), and combinations thereof, and one or more buffer-adjusted anion(s) at a WHSV at least about 0.3 hr^{-1},

thereby producing a diene product that comprises one or more diene(s) at a one-pass yield greater than about 73 mol%.

50. A method according to claim 49, wherein said crotyl alcohol is in a mixture comprising about 1 ppm to about 93 wt-% water.

51. The method according to claim 50, wherein said mixture comprises about 5 wt-% to about 70 wt-% water.

52. A method according to claim 49, wherein said crotyl alcohol is bio-crotyl alcohol.

53. A method according to claim 49, wherein said one or more diene(s) is 1,3-butadiene.

54. A method according to claim 49, wherein the molar selectivity of said one or more diene(s) production is greater than about 95%.

55. A method according to claim 49, wherein the molar selectivity of said one or more diene(s) production is about 90% to about 99%.

56. A method according to claim 49, wherein said inorganic support comprises γ-alumina.

57. A method according to claim 49, wherein said catalyst is further modified by treatment with at least one organosilane.

58. The method according to claim 57, wherein said organosilane comprises an alkoxysilane.

59. A method according to claim 49, further comprising providing at least one carrier gas.

60. A method according to claim 49, wherein the Group 2 element is Ca.

61. A method according to claim 49, wherein the buffer-adjusted anion is selected from SO_4^{-2}, $H_2PO_4^{-1}$, and mixtures thereof.

62. A method of producing crotyl alcohol, comprising growing a microorganism in a growth medium under fermentation conditions suitable for production of crotyl alcohol.

63. A method according to claim 62, wherein the microorganism expresses a native

enzyme that can produce crotyl alcohol from a substrate in the growth medium.

64. A method according to claim 63, wherein the enzyme is an alcohol and/or aldehyde dehydrogenase.

65. A method according to claim 63, wherein the enzyme is an acyl-CoA reductase.

66. A method according to claim 63, wherein the substrate is crotonaldehyde.

67. A method according to claim 63, wherein the crotyl alcohol is produced from upstream biosynthetic intermediates comprising crotonic acid, crotonyl-CoA and/or other intermediates in the butanol/butanoate pathway.

68. A method according to claim 63, wherein the native enzyme is part of a native butanoate/butanol, fatty acid, amino acid degradation, or related metabolic pathway in the microorganism.

69. A method according to claim 68, wherein the metabolic pathway comprises an enzyme of a glycolytic or pentose phosphate pathway that converts glucose and/or xylose to acetyl-CoA, a thiolase enzyme that converts acetyl-CoA to acaetoacetyl-CoA, a 3-hydroxy butyryl CoA dehydrogenase enzyme that converts acetoacetyl-CoA to 3-hydroxybutyryl-CoA, a crotonase enzyme that converts 3-hydroxybutyryl-CoA to crotonyl-CoA, an aldehyde dehydrogenase enzyme that converts crotonyl-CoA to crotonaldehyde, and an alcohol dehydrogenase enzyme that converts crotonaldehyde to crotyl alcohol._

70. A method according to claim 62, wherein the microorganism is a *Clostridium* strain.

71. A method according to claim 70, wherein the *Clostridium* microorganism expresses an enzyme that converts crotonaldehyde to crotyl alcohol.

72. A method according to claim 70, wherein the *Clostridium* microorganism expresses an enzyme that converts crotonyl-CoA to crotonaldehyde or crotyl alcohol.

73. A method according to claim 71, wherein the enzyme that converts crotonaldehyde to crotyl alcohol is a native enzyme in the *Clostridium* microorganism.

74. A method according to claim 72, wherein the enzyme that converts crotonyl-CoA to crotonaldehyde or crotyl alcohol is a native enzyme in the *Clostridium* microorganism.

75. A method according to claim 71, wherein the enzyme is an alcohol and/or aldehyde dehydrogenase.

76. A method according to claim 72, wherein the enzyme is an acyl-CoA reductase that

converts crotonyl-CoA to crotyl alcohol without intervening additional enzymatic activities

77. A method according to claim 62, wherein the growth medium comprises one or more substances that increase production of crotyl alcohol in comparison to a growth medium that does not comprise the one or more substances.

78. A method according to claim 77, wherein the one or more substances comprise one or more co-factors of enzymes in a butanoate/butanol pathway in the microorganism.

79. A method according to claim 78, wherein the one or more co-factors include one or more of Mn, Fe, NADPH, and NADP.

80. A method according to claim 78, wherein the one or more substances modifies the activity of one or more native enzyme(s) in the microorganism, thereby increasing crotyl alcohol production.

81. A method according to claim 80, wherein bcd is inhibited by the one or more substances in the growth medium.

82. A method according to claim 80, wherein adhE and adh2 are activated by the one or more substances in the growth medium.

83. A method according to claim 77, wherein the one or more substances in the growth medium comprises one or more divalent metal ion(s), iodoacetamide, myristoyl-CoA, N-ethylmaleimide, and/or palmitoyl-CoA.

84. A method according to claim 83, wherein the one or more divalent metal ion(s) is selected from selected from Ca, Co, Zn, and Mn, and combinations thereof.

85. A method according to claim 62, wherein the growth medium comprises carbohydrate molecules produced by hydrolysis of lignocellulosic biomass.

86. An engineered *Clostridium* strain that produces a greater amount of crotyl alcohol than the parent strain from which it was derived.

87. A *Clostridium* strain according to claim 86, wherein said strain has been engineered to comprise a reduced level or activity of butyryl-CoA dehydrogenase in comparison to the parent strain from which it was derived.

88. A *Clostridium* strain according to claim 87, wherein one or more enzyme(s) of a crotyl alcohol biosynthetic pathway is overexpressed.

89. A *Clostridium* strain according to claim 88, wherein the one or more enzyme(s) of

crotyl alcohol biosynthesis comprises an enzyme of a glycolytic or pentose phosphate pathway that converts glucose and/or xylose to acetyl-CoA, a thiolase enzyme that converts acetyl-CoA to acaetoacetyl-CoA, a 3-hydroxy butyryl CoA dehydrogenase enzyme that converts acetoacetyl-CoA to 3-hydroxybutyryl-CoA, a crotonase enzyme that converts 3-hydroxybutyryl-CoA to crotonyl-CoA, an aldehyde dehydrogenase enzyme that converts crotonyl-CoA to crotonaldehyde, and/or an alcohol dehydrogenase enzyme that converts crotonaldehyde to crotyl alcohol.

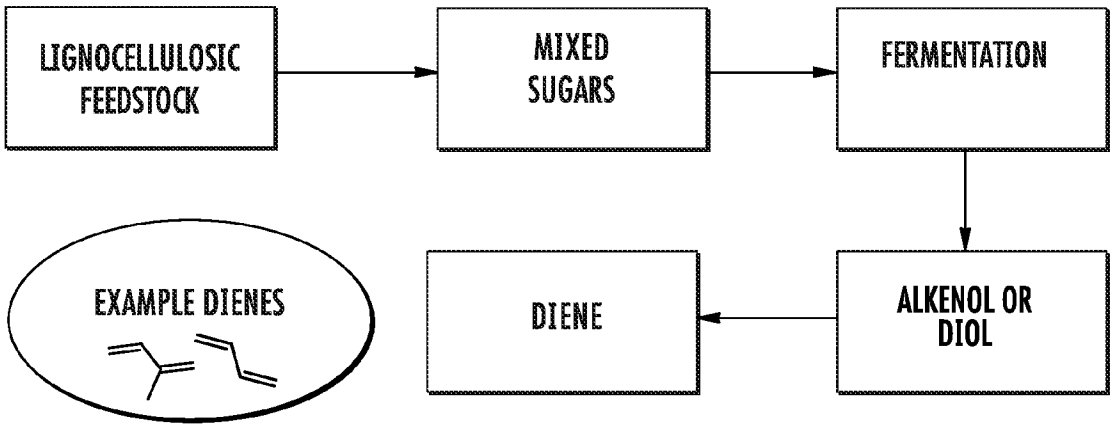
90. A *Clostridium* strain according to claim 89, wherein the one or more enzyme(s) of crotyl alcohol biosynthesis comprises at least one alcohol dehydrogenase.

91. A *Clostridium* strain according to claim 87, wherein said strain is an SiHybrid in which butyryl-CoA dehydrogenase activity is downregulated in comparison to the parent strain from which it was derived.

92. A *Clostridium* strain according to claim 87, wherein butyryl-CoA dehydrogenase has been inactivated using a targetron gene knockout system.

93. A method of producing crotyl alcohol, comprising growing the *Clostridium* strain according to claim 86 in a growth medium under fermentation conditions suitable for production of crotyl alcohol.

94. A method according to claim 93, wherein the growth medium comprises carbohydrate molecules produced by hydrolysis of lignocellulosic biomass.



NON-FOOD BIOMASS CONVERSION TO DIENES

FIG. 1

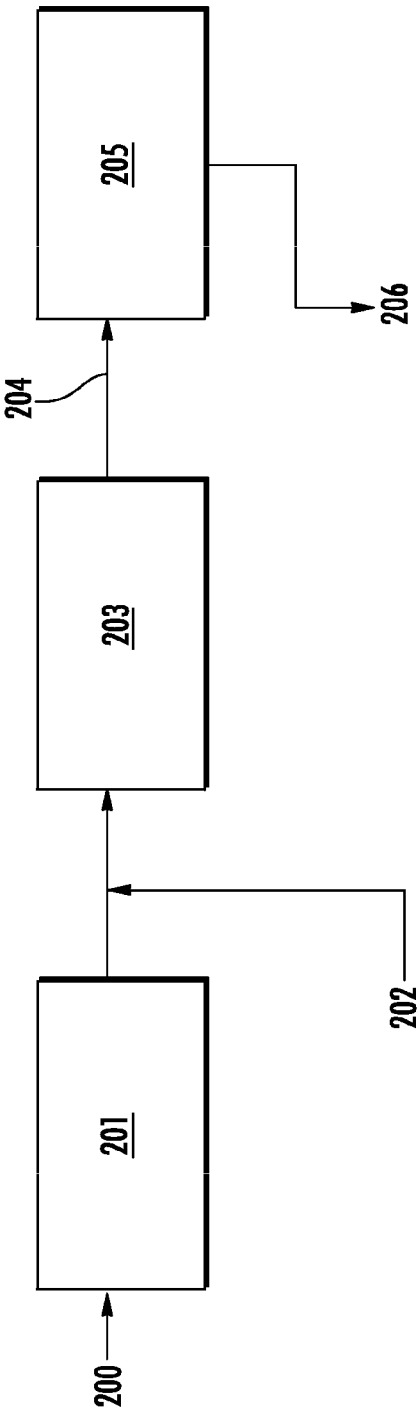


FIG. 2

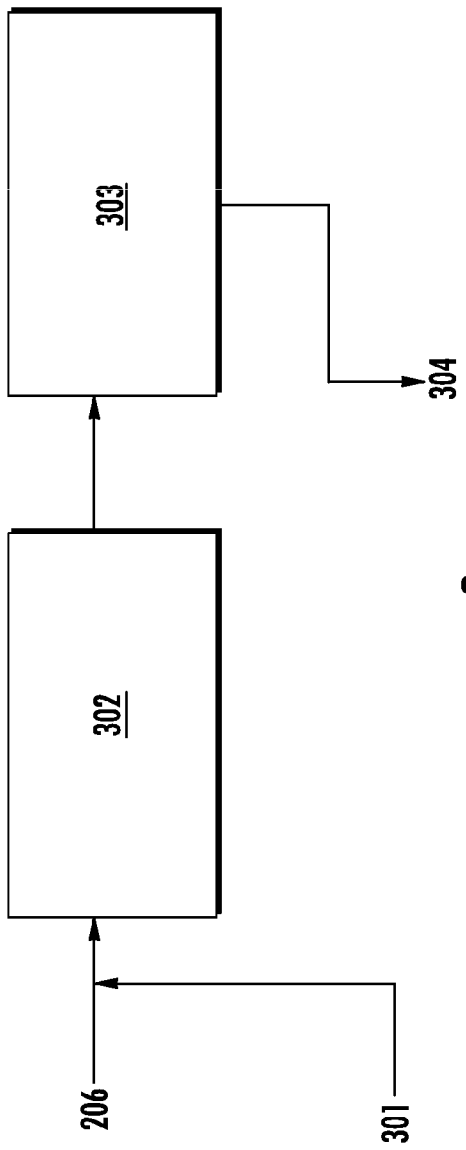


FIG. 3

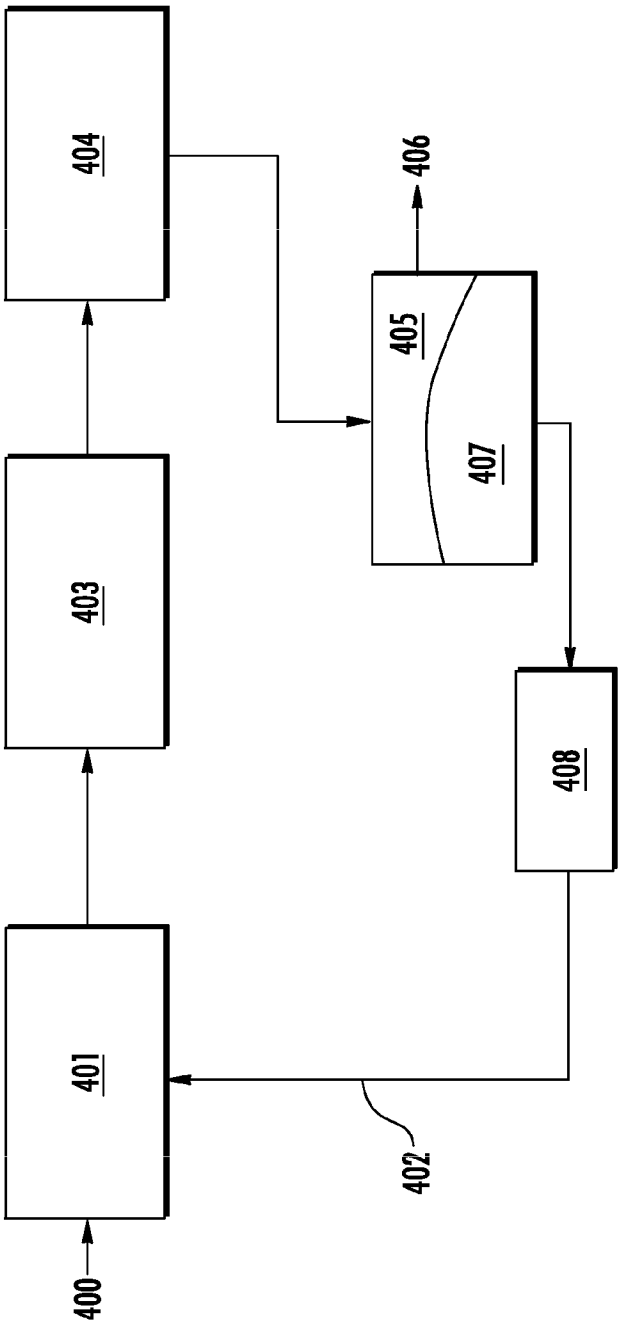


FIG. 4

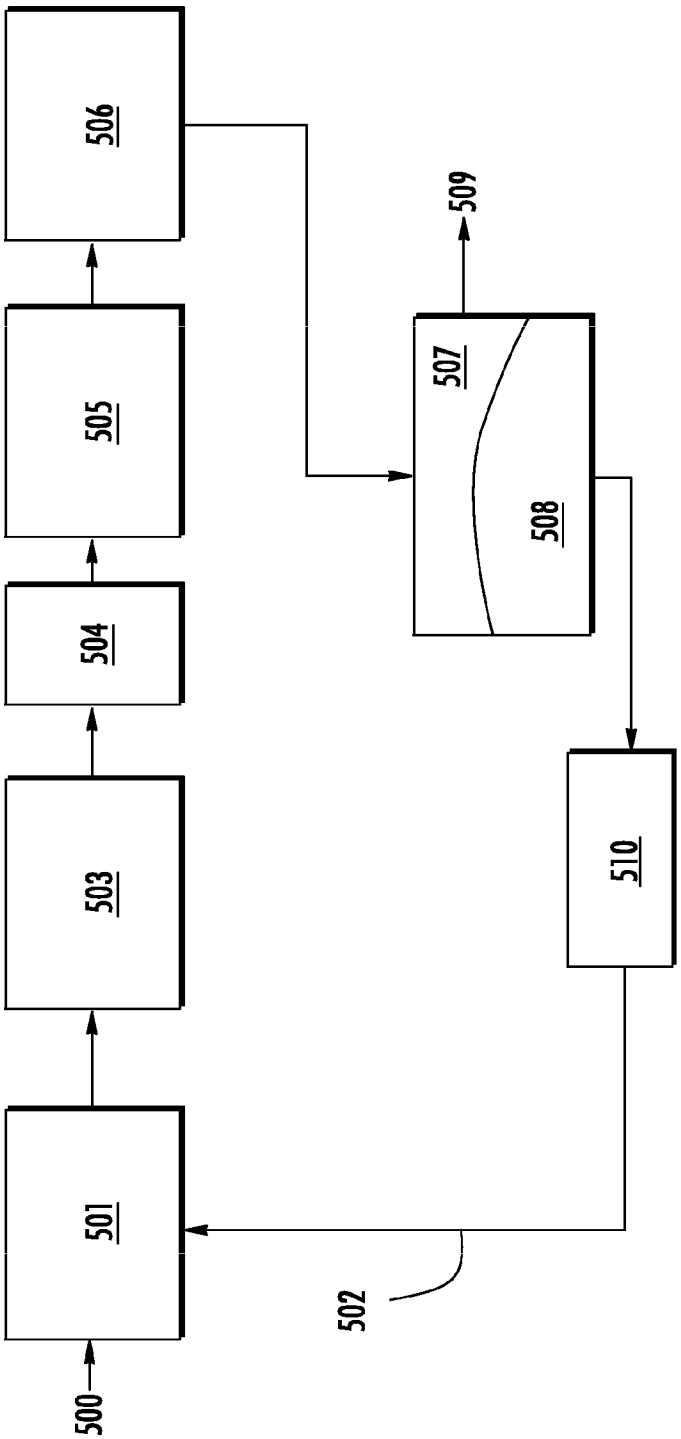


FIG. 5

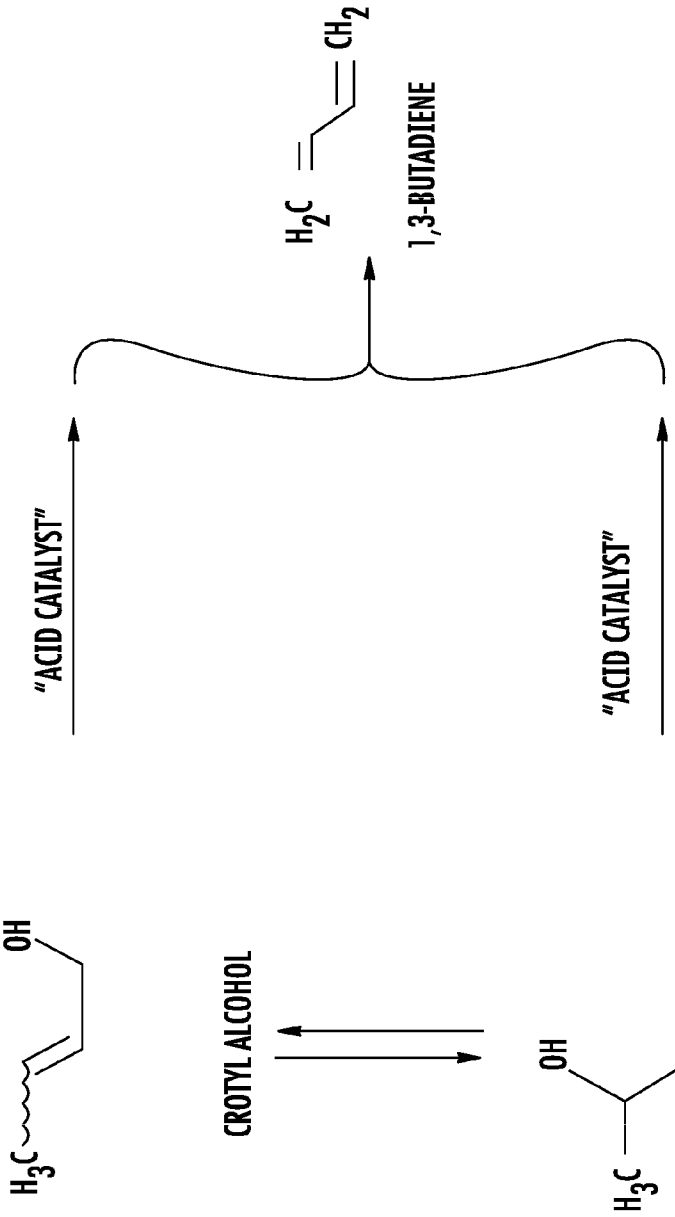

"ACID CATALYST"
"ACID CATALYST"
1,3-BUTADIENE
CROTYL ALCOHOL
3-BUTENE-2-ol

FIG. 6

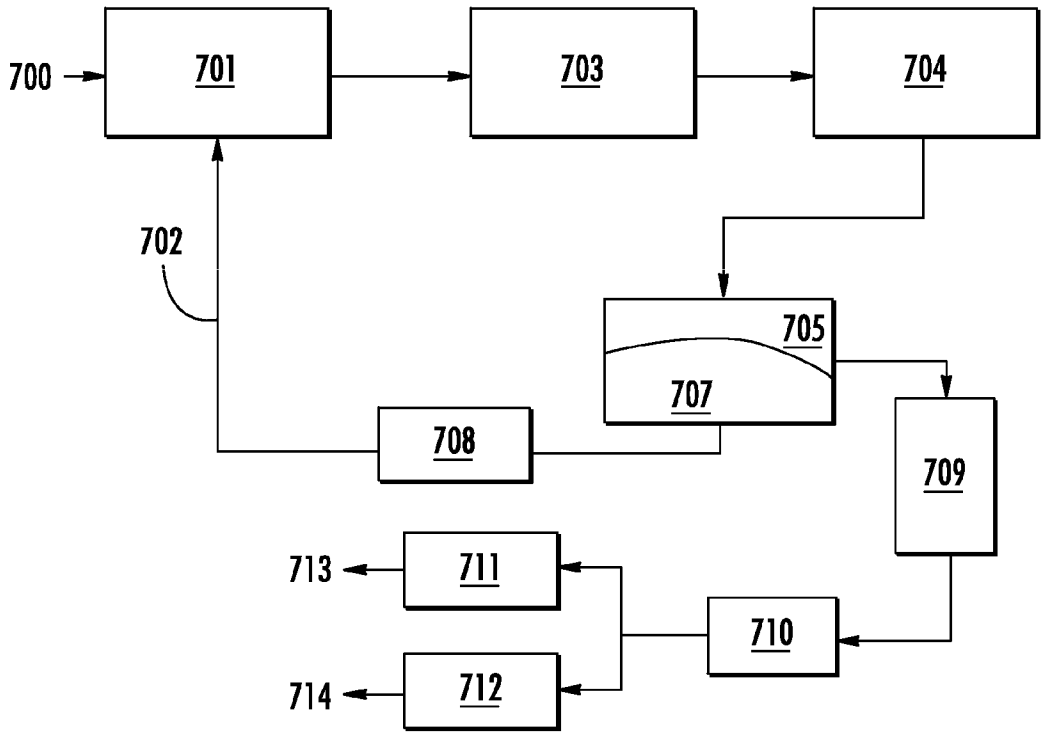


FIG. 7

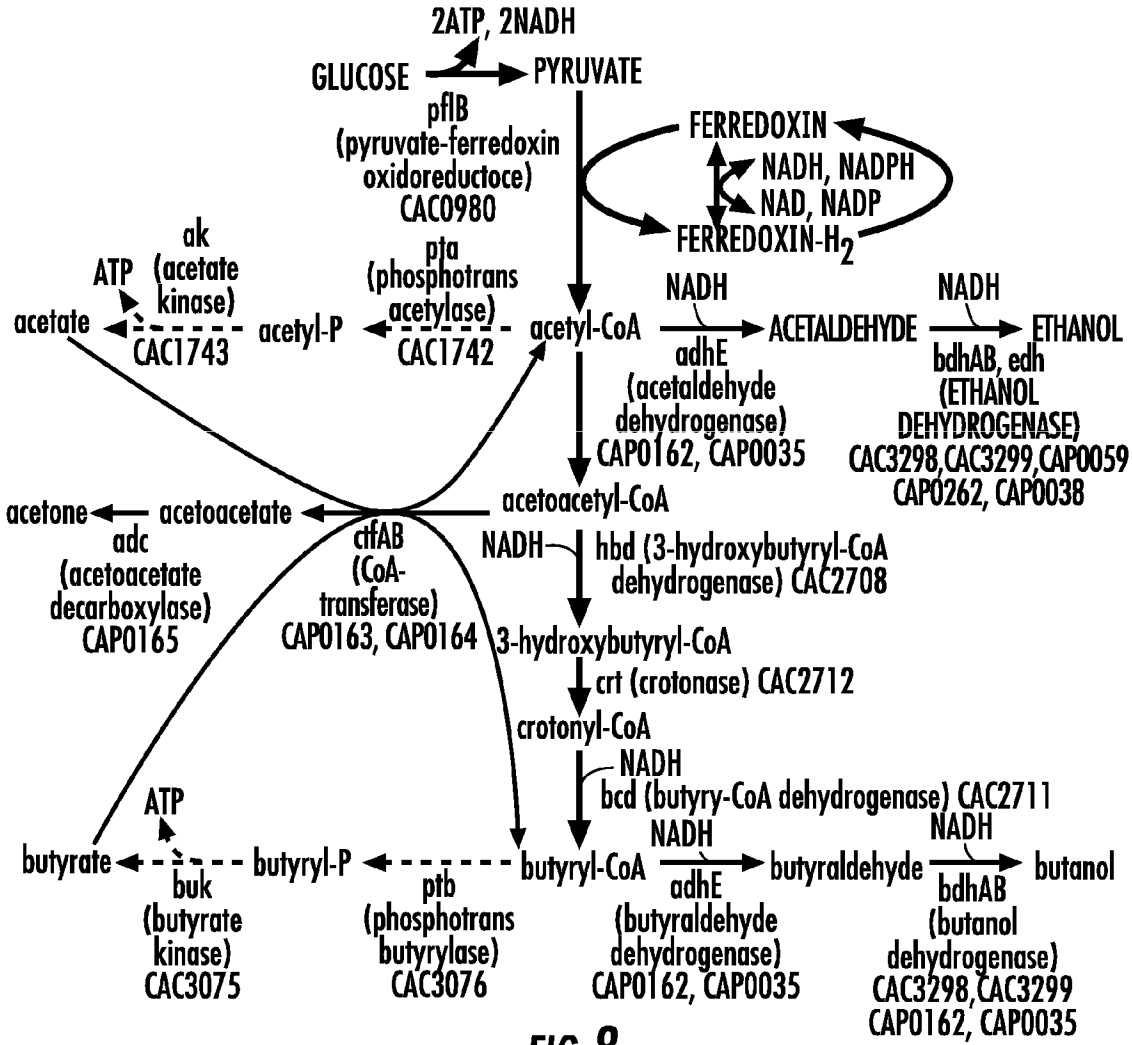
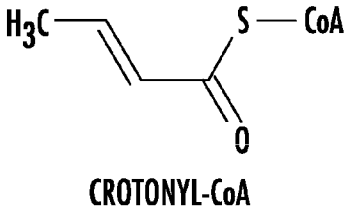


FIG. 8



CROTONYL-CoA

FIG. 9

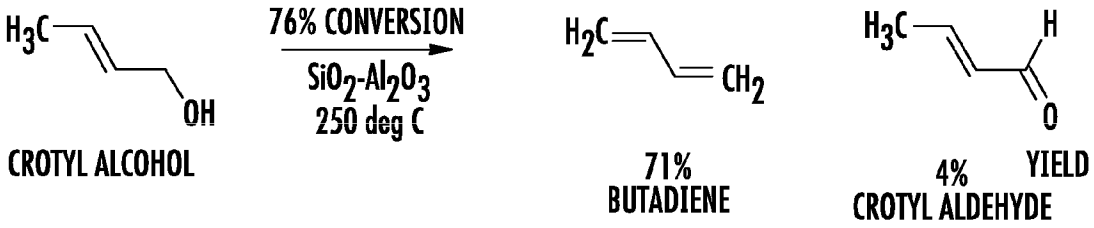

H3C
OH
CROTYL ALCOHOL
76% CONVERSION
SiO2-Al2O3
250 deg C
H2C
CH2
71%
BUTADIENE
H3C
H
O
4%
YIELD
CROTYL ALDEHYDE

FIG. 10

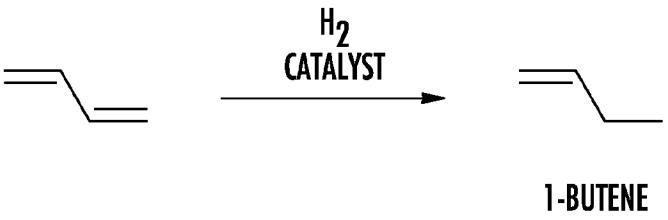

H2
CATALYST
1-BUTENE

FIG. 11

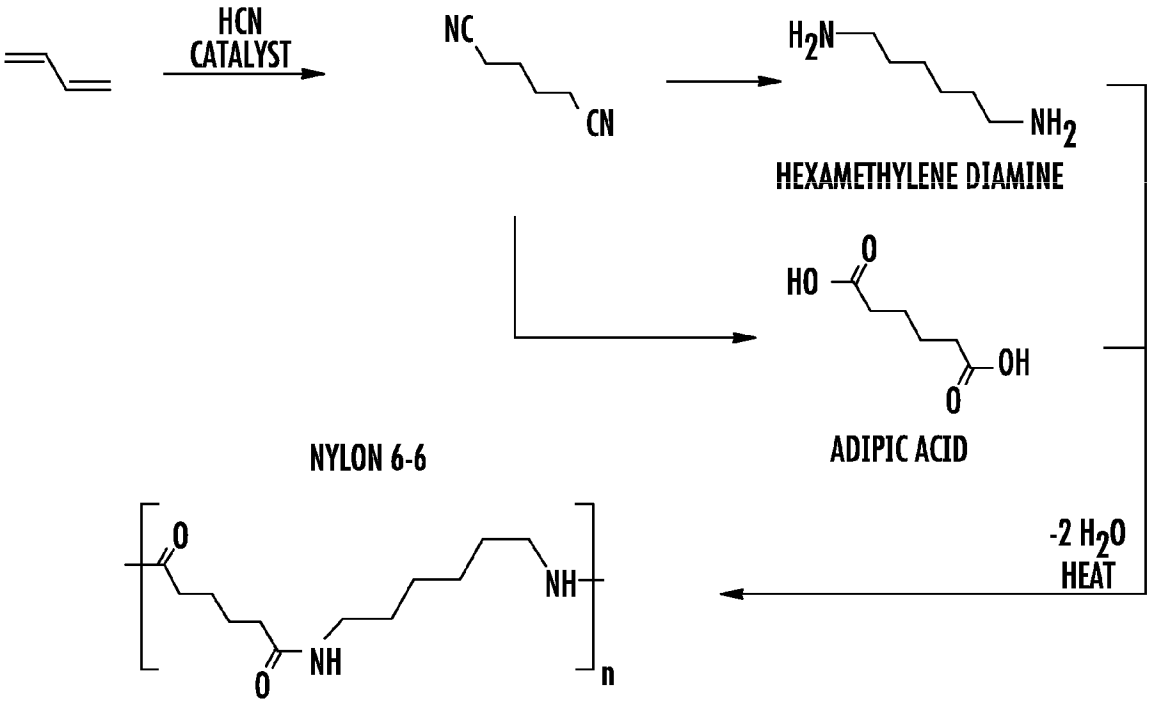

HCN
CATALYST
NC
CN
H_2N
NH_2
HEXAMETHYLENE DIAMINE
HO
O
OH
O
ADIPIC ACID
-2 H_2O
HEAT
NYLON 6-6
O
NH
O
NH
n

FIG. 12

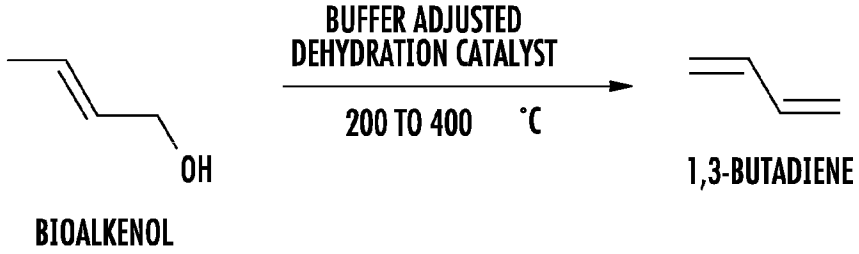

BUFFER ADJUSTED
DEHYDRATION CATALYST
200 TO 400 °C
OH
BIOALKENOL
1,3-BUTADIENE

FIG. 13

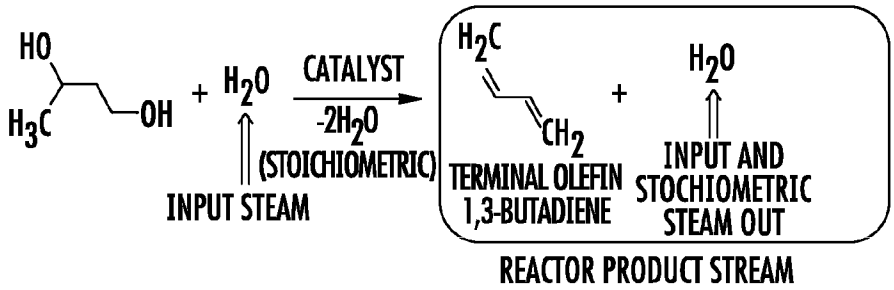

HO
H3C
OH
+ H2O
INPUT STEAM
CATALYST
-2H2O
(STOICHIOMETRIC)
H2C
CH2
TERMINAL OLEFIN
1,3-BUTADIENE
+
H2O
INPUT AND
STOCHIOMETRIC
STEAM OUT
REACTOR PRODUCT STREAM

FIG. 14

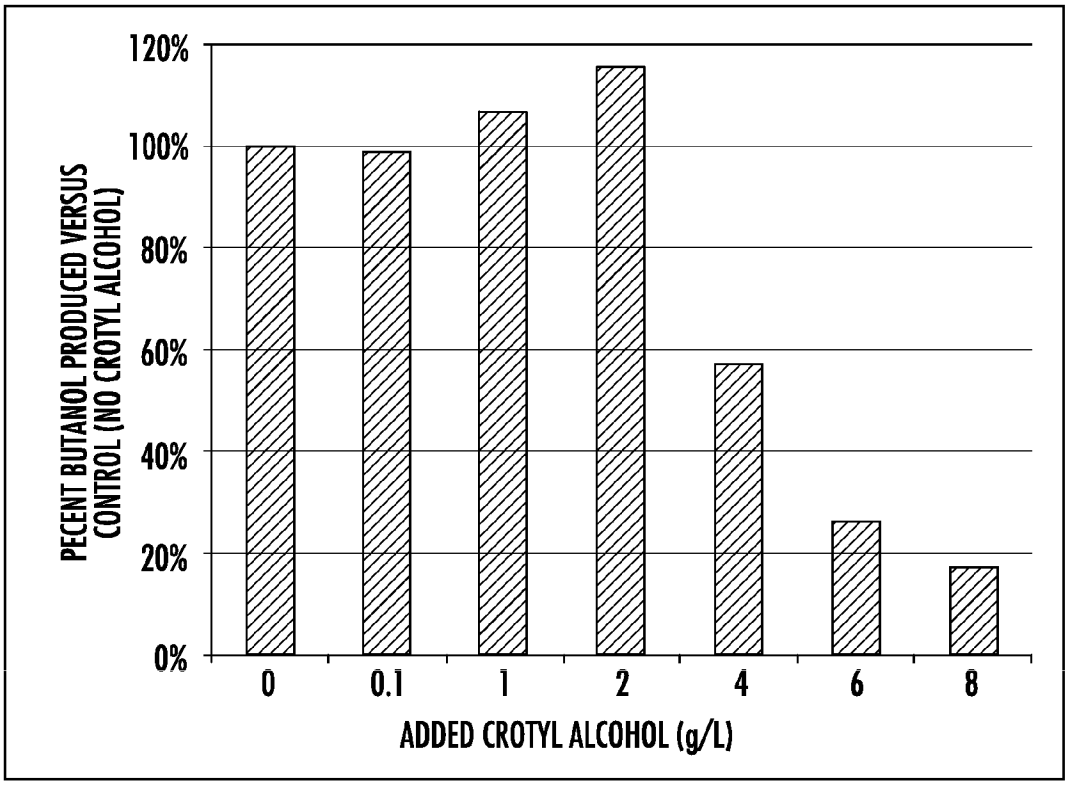

PECENT BUTANOL PRODUCED VERSUS CONTROL (NO CROTYL ALCOHOL)
120%
100%
80%
60%
40%
20%
0%
0
0.1
1
2
4
6
8
ADDED CROTYL ALCOHOL (g/L)

FIG. 15

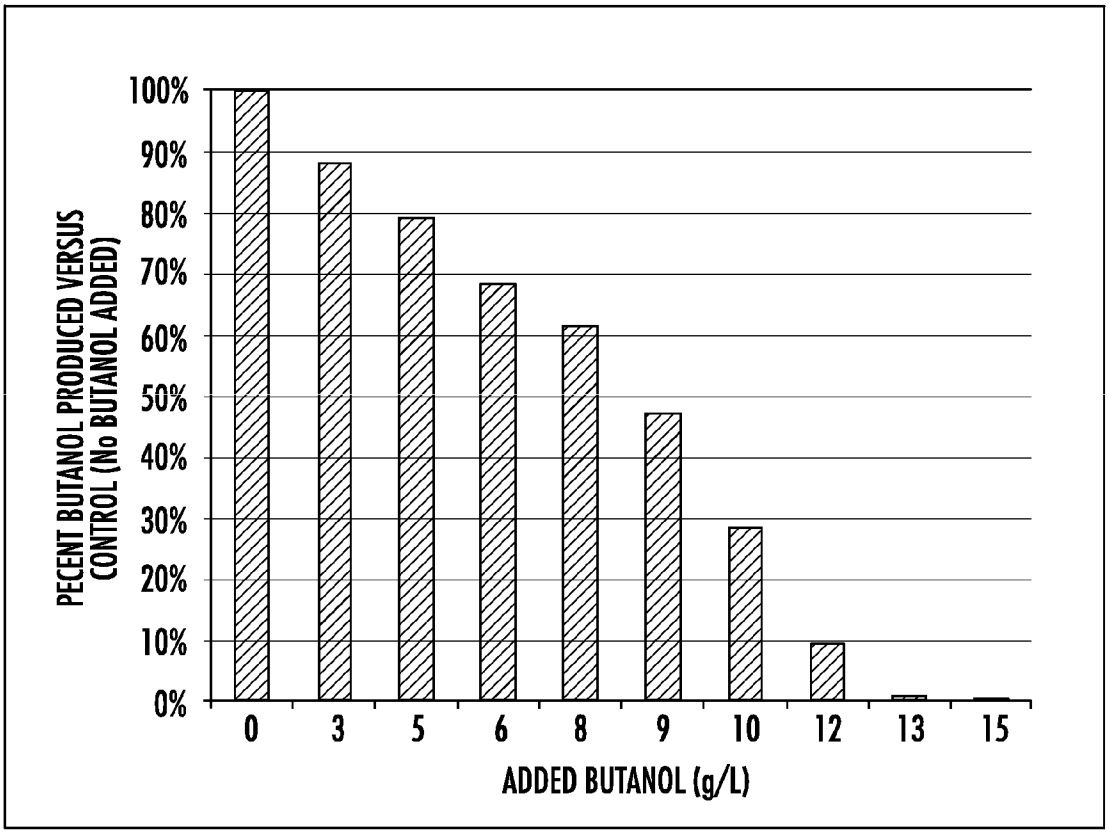

PECENT BUTANOL PRODUCED VERSUS CONTROL (No BUTANOL ADDED)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
3
5
6
8
9
10
12
13
15
ADDED BUTANOL (g/L)

FIG. 16

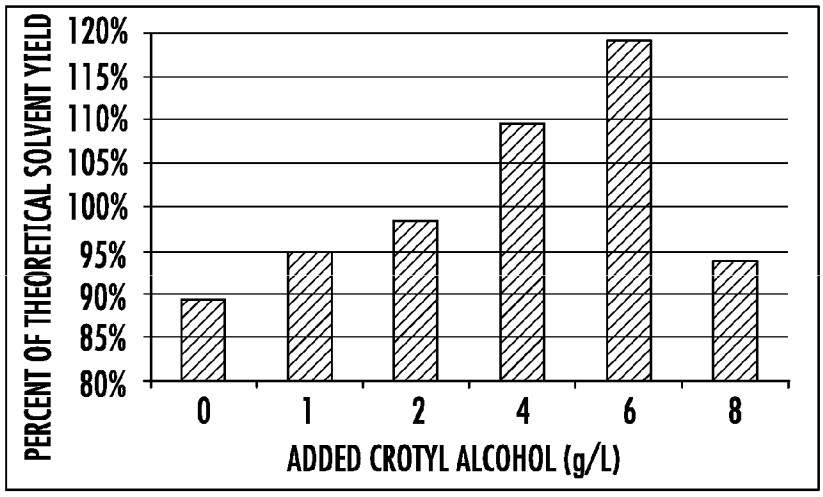

PERCENT OF THEORETICAL SOLVENT YIELD
120%
115%
110%
105%
100%
95%
90%
85%
80%
0
1
2
4
6
8
ADDED CROTYL ALCOHOL (g/L)

FIG. 17

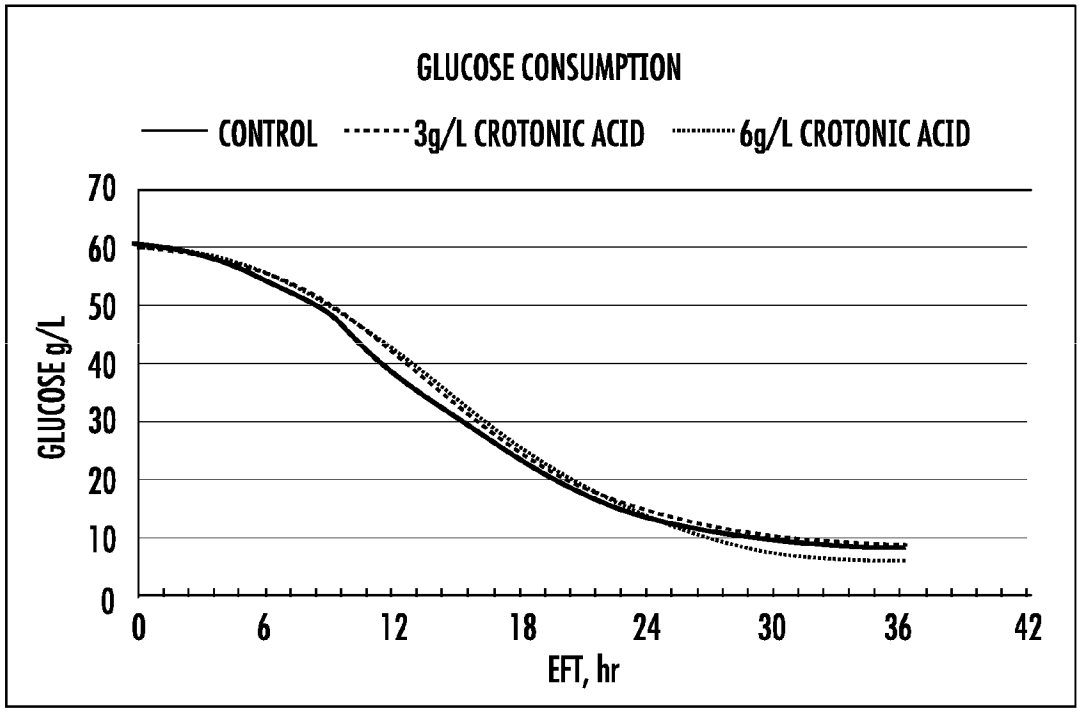

GLUCOSE CONSUMPTION
CONTROL
3g/L CROTONIC ACID
6g/L CROTONIC ACID
GLUCOSE g/L
70
60
50
40
30
20
10
0
0
6
12
18
24
30
36
42
EFT, hr

FIG. 18

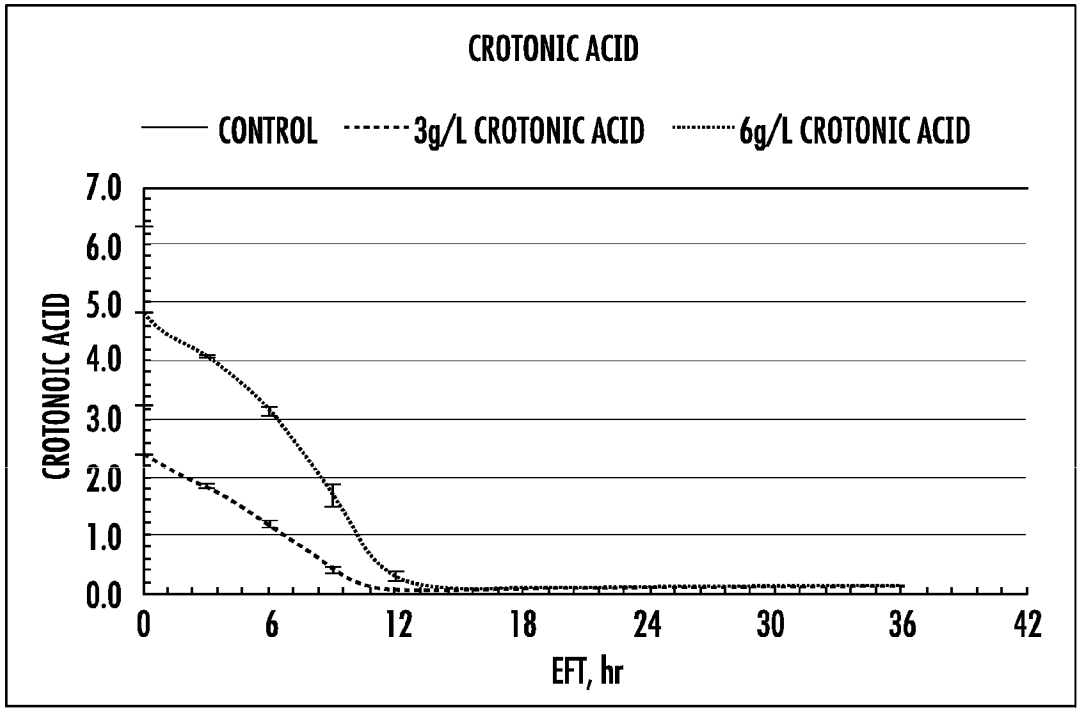

CROTONIC ACID
CONTROL
3g/L CROTONIC ACID
6g/L CROTONIC ACID
CROTONOIC ACID
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
6
12
18
24
30
36
42
EFT, hr

FIG. 19

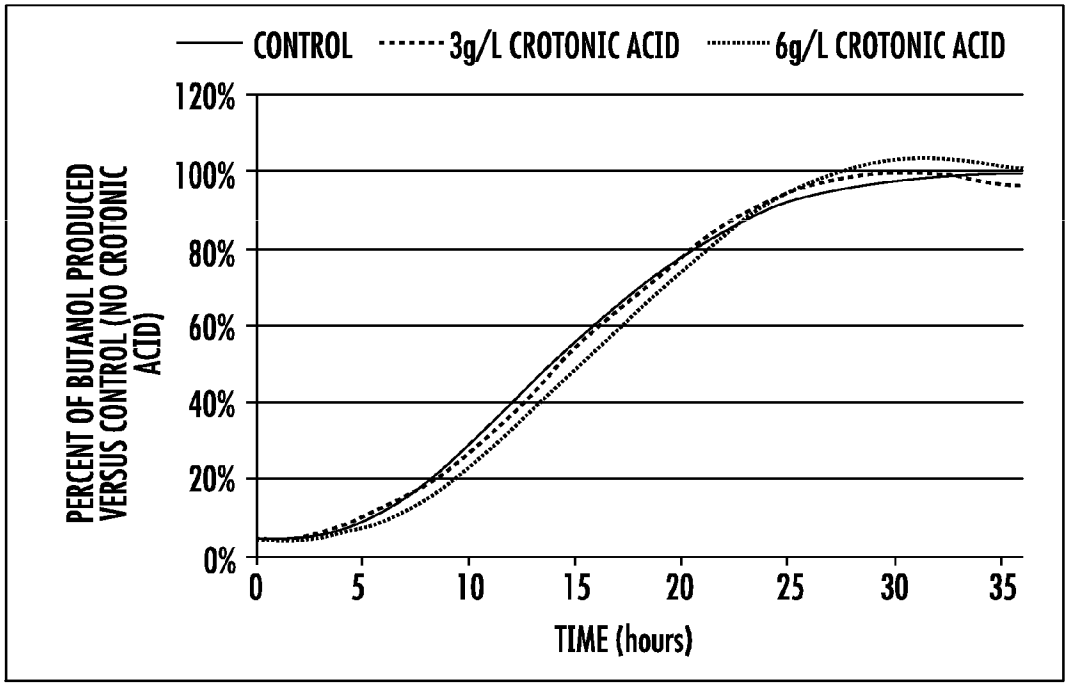

CONTROL
3g/L CROTONIC ACID
6g/L CROTONIC ACID
PERCENT OF BUTANOL PRODUCED VERSUS CONTROL (NO CROTONIC ACID)
120%
100%
80%
60%
40%
20%
0%
0
5
10
15
20
25
30
35
TIME (hours)

FIG. 20

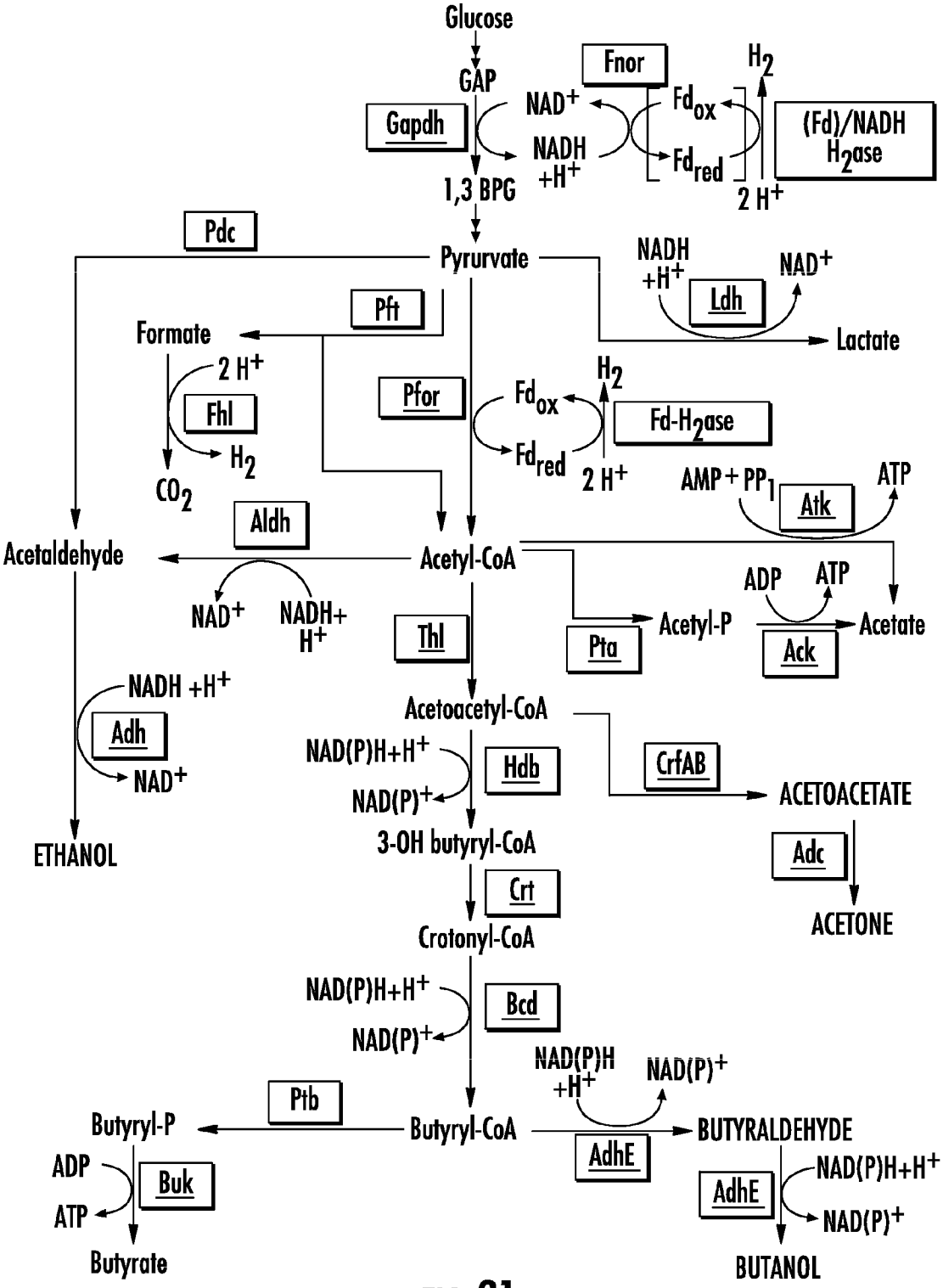

Glucose
GAP
Gapdh
NAD+
NADH +H+
Fnor
Fdox
Fdred
H2
2 H+
(Fd)/NADH H2ase
1,3 BPG
Pdc
Pyrurvate
NADH +H+
NAD+
Ldh
Lactate
Pft
Formate
2 H+
Fhl
H2
CO2
Pfor
Fdox
Fdred
H2
2 H+
Fd-H2ase
AMP + PPi
Atk
ATP
Aldh
Acetaldehyde
Acetyl-CoA
NAD+
NADH+ H+
Thl
Pta
Acetyl-P
ADP
ATP
Ack
Acetate
NADH +H+
Adh
NAD+
ETHANOL
Acetoacetyl-CoA
NAD(P)H+H+
NAD(P)+
Hdb
CrfAB
ACETOACETATE
Adc
ACETONE
3-OH butyryl-CoA
Crt
Crotonyl-CoA
NAD(P)H+H+
NAD(P)+
Bcd
NAD(P)H +H+
NAD(P)+
Ptb
Butyryl-P
Butyryl-CoA
AdhE
BUTYRALDEHYDE
ADP
ATP
Buk
Butyrate
AdhE
NAD(P)H+H+
NAD(P)+
BUTANOL

FIG. 21

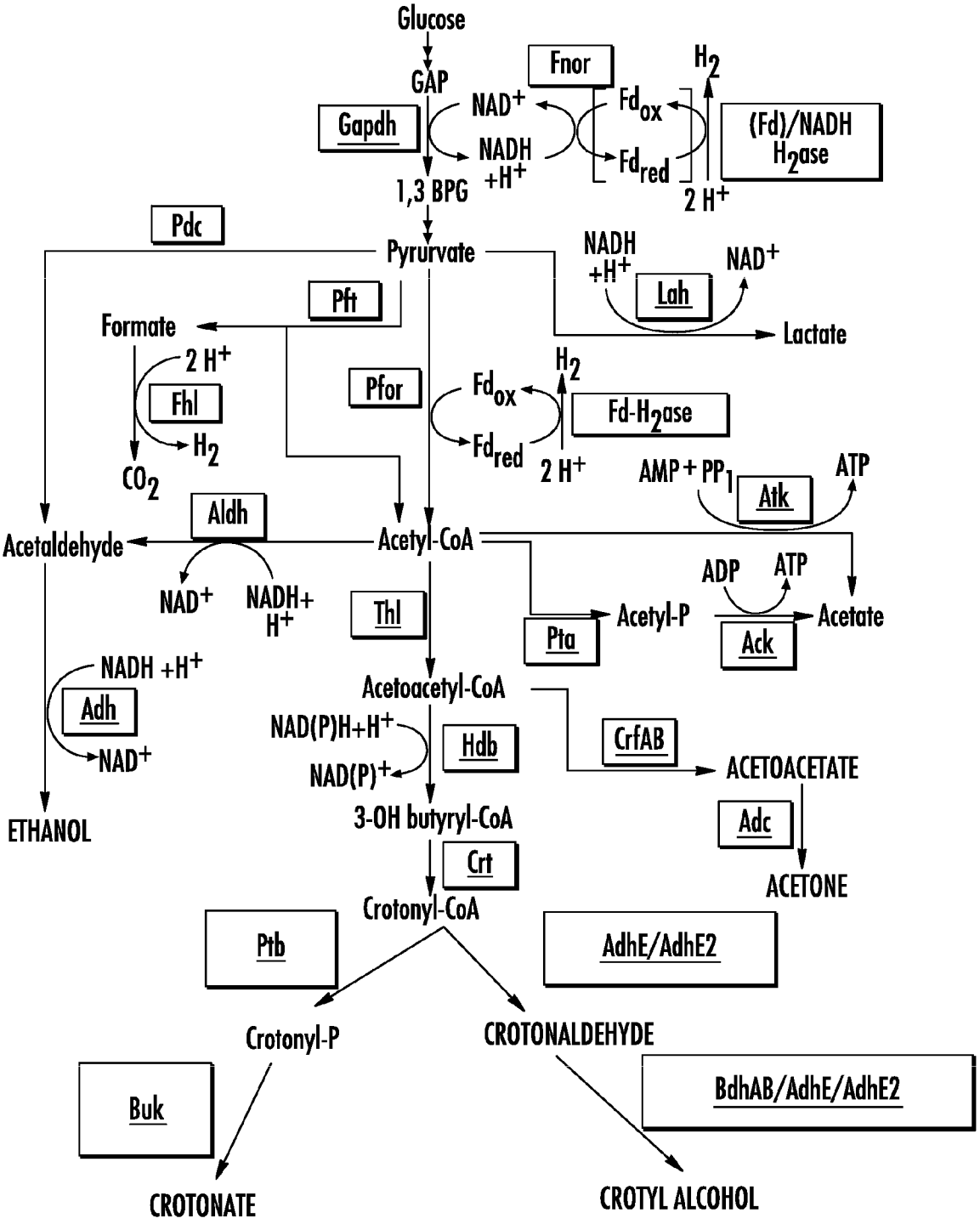

Glucose
GAP
Gapdh
NAD+
NADH +H+
1,3 BPG
Fnor
Fdox
Fdred
H2
2 H+
(Fd)/NADH H2ase
Pdc
Pyrurvate
NADH +H+
NAD+
Lah
Lactate
Pft
Formate
2 H+
Fhl
H2
CO2
Pfor
Fdox
Fdred
H2
2 H+
Fd-H2ase
AMP + PPi
Atk
ATP
Aldh
Acetaldehyde
Acetyl-CoA
NAD+
NADH+ H+
Thl
ADP
ATP
Acetyl-P
Pta
Ack
Acetate
NADH +H+
Adh
NAD+
ETHANOL
Acetoacetyl-CoA
NAD(P)H+H+
NAD(P)+
Hdb
CrfAB
ACETOACETATE
Adc
ACETONE
3-OH butyryl-CoA
Crt
Crotonyl-CoA
Ptb
AdhE/AdhE2
Crotonyl-P
CROTONALDEHYDE
Buk
BdhAB/AdhE/AdhE2
CROTONATE
CROTYL ALCOHOL

FIG. 22

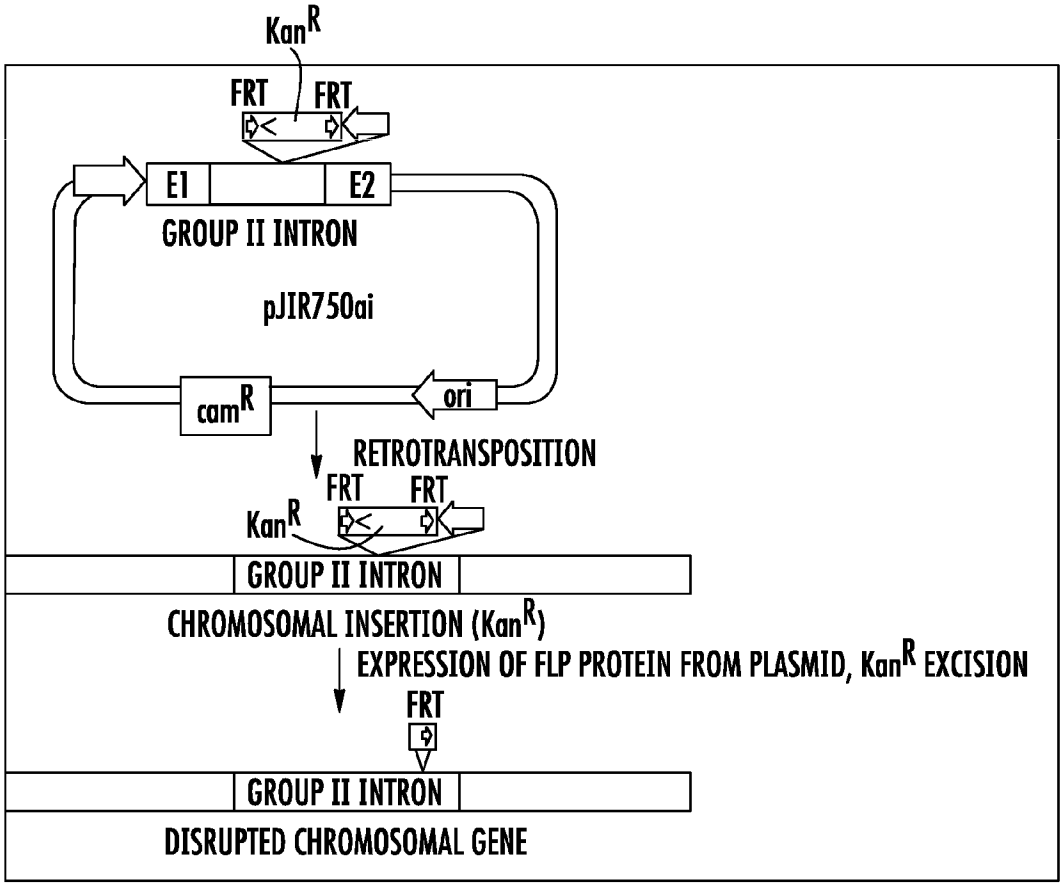

Kan^R
FRT
FRT
E1
E2
GROUP II INTRON
pJIR750ai
cam^R
ori
RETROTRANSPOSITION
FRT
FRT
Kan^R
GROUP II INTRON
CHROMOSOMAL INSERTION (Kan^R)
EXPRESSION OF FLP PROTEIN FROM PLASMID, Kan^R EXCISION
FRT
GROUP II INTRON
DISRUPTED CHROMOSOMAL GENE

FIG. 23

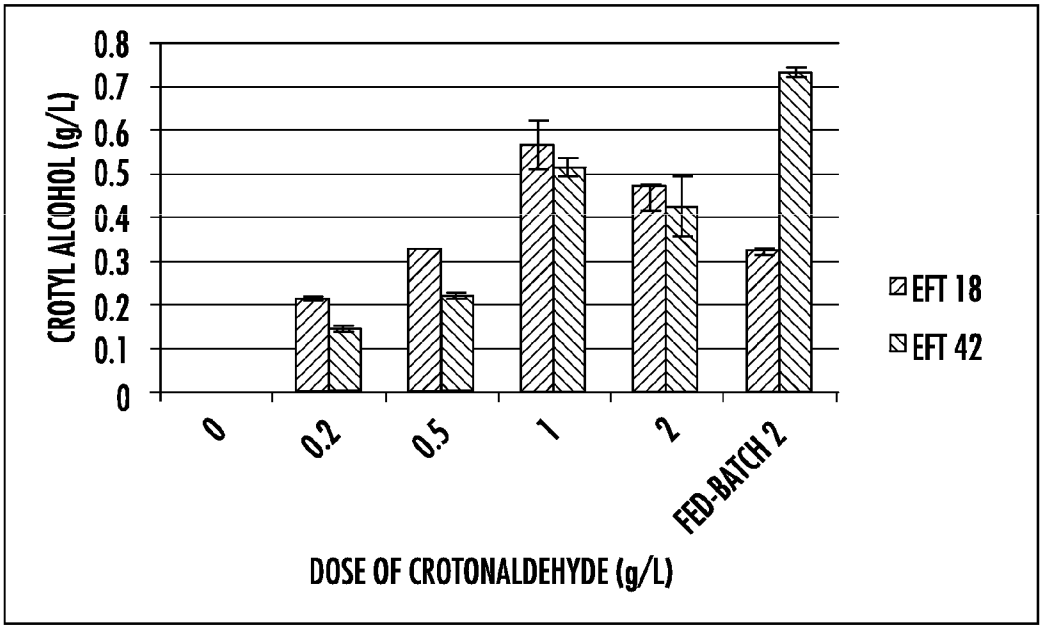

CROTYL ALCOHOL (g/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.5
1
2
FED-BATCH 2
DOSE OF CROTONALDEHYDE (g/L)
EFT 18
EFT 42

FIG. 24

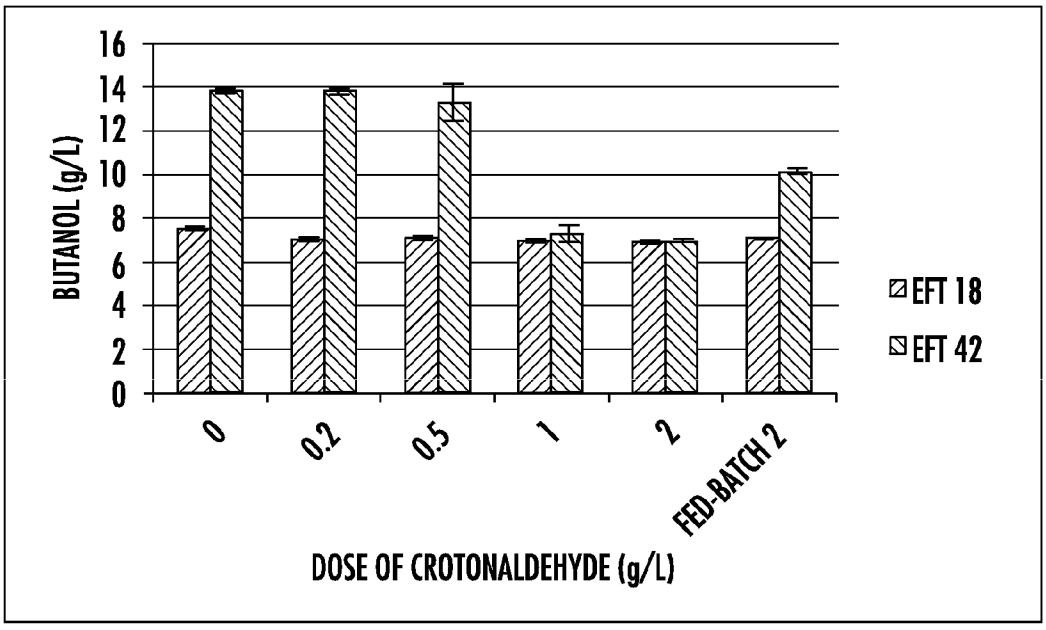

BUTANOL (g/L)
16
14
12
10
8
6
4
2
0
0
0.2
0.5
1
2
FED-BATCH 2
DOSE OF CROTONALDEHYDE (g/L)
EFT 18
EFT 42

FIG. 25

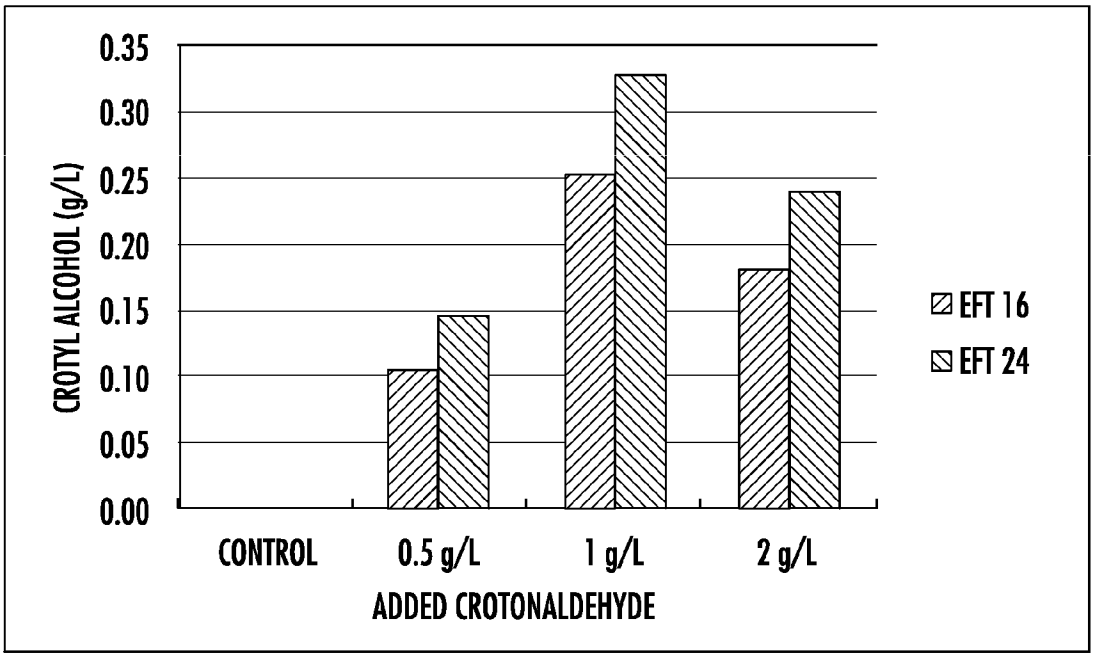

0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
CROTYL ALCOHOL (g/L)
CONTROL
0.5 g/L
1 g/L
2 g/L
ADDED CROTONALDEHYDE
EFT 16
EFT 24

FIG. 26

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 15/11371

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01J 29/06, C07C 2/12, C07C 5/32, C07C 11/167 (2015.01)
CPC - B01J 29/06, C07C 2/12, C07C 5/32, C07C 5/321, C07C 11/167
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8)- B01J 29/06, C07C 2/12, C07C 5/32, C07C 11/167 (2015.01);
CPC- B01J 29/06, C07C 2/12, C07C 5/32, C07C 5/321, C07C 11/167

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC- 208/187, 208/49, 208/DIG2, 585/252, 585/475, 585/481, 585/615, 585/664;
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Pub West (US EP JP WO), Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar, Free Patents Online; search terms: dehydrate, dehydrogenate, hydroform, diene, butadiene, alkenol, diol, crotyl, alcohol, catalyst, inorganic, alumina, organosilane, alkoxysilane, chlorosilane, calcium, diesel, jet, fuel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/0225466 A1 (BURK et al.) 06 September 2012 (06.09.2012), para [0007], [0045], [0046], [0243]	1-31
Y	US 2007/0144939 A1 (ZONES et al.) 28 June 2007 (28.06.2007), para [0040], [0046], [0065]-[0068], [0102], [0114], [0116], [0139]	1-31
Y	US 5,498,811 A (PEREGO et al.) 12 March 1996 (12.03.1996), col 2, ln 20-30; col 3, ln 13-17; col 3, ln 43-61	14, 19, 23-28
Y	US 5,476,982 A (ROBBINS et al.) 19 December 1995 (19.12.1995), col 1, ln 35-50; col 2, ln 18-57; col 5, ln 9-46; col 12, ln 8-10	15-17
Y	US 3,835,199 A (SCHWARTZ JR et al.) 10 September 1974 (10.09.1974), col 1, ln 48 to col 6, ln 60	1-31
Y	US 2,407,291 A (QUATTLEBAUM et al.) 10 September 1946 (10.09.1946), col 2, ln 17 to col 6, ln 75	1-31

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 2015 (30.05.2015)	24 JUN 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 15/11371

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

-- Please See Extra Sheet --

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-31

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2015)

Continued from Box No. III, Observations where unity of invention is lacking,

The only feature shared by Groups I, III, IV, and V that would otherwise unify the groups is one or more Group 2 element(s). However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by Zones.

Zones discloses one or more Group 2 element(s) (para [0114], Group II.).

The only feature shared by Groups I and V that would otherwise unify the groups is one or more buffer-adjusted anion(s) at a WHSV at least about 0.3 hr-1. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by Zones.

Zones discloses one or more buffer-adjusted anion(s) (para [0040], [0046]) at a WHSV at least about 0.3 hr-1 (para [0040], [0069], [0108], SSZ-74 catalysts comprise SDA dication for production of halide to hydroxide ions... superscript 5 WHSV, having values of about 0.1 per hour.)

The only feature shared by Groups III, IV, and V that would otherwise unify the groups is at least one inorganic support. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by Zones.

Zones discloses at least one inorganic support (para [0062], matrix materials such as clay, silica, metal oxides.).

The only feature shared by Groups V, VI, and VII that would otherwise unify the groups is crotyl alcohol. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by US 2013/0109064 A1 to Osterhout, et al. (hereinafter 'Osterhout').

Osterhout discloses crotyl alcohol (para [0012], [0025], [0105]).

As the technical feature was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I-VII therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:57
S2	69	(("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S3	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S4	69	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S5	2	"2016007196".pn.	US-PGPUB; USPAT; USOCR; FPRS; EPO	OR	OFF	2019/07/31 11:33
S6	9189	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:43
S7	1392	(natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:45
S8	23	S6 and S7 and alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 12:46
S9	9170	(method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S10	684	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and dehydration	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S11	378	S10 and (natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:51
S12	125	S11 and (alkene or octene or pentene	US-PGPUB;	OR	OFF	2019/07/31

		or hexene or heptene or nonene or decene or dodecene)	USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			13:02
S13	125	S12 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:03
S14	9170	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S15	1219	S14 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:05
S16	1175	S15 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S17	55	S14 and (terminal with (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:07
S18	3	("20050006997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:29
S19	3	("20050069997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:30
S20	5912	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:35
S21	2221	S20 and (natural or plant or vegetable or ferment$4 or biomass)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:40
S22	312	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and (peracid or formic of acetic) and (hydrogen adj peroxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S23	308	S22 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S24	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:51

		acetic) with (hydrogen adj peroxide))				
S25	3031	C07C29/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:15
S26	5809	C07C31/20.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S27	0	C07C33/25.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S28	3127	C07C33/025.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S29	18997	B01J21/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S30	16230	B01J37/08.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:18
S31	4501	B01J23/06.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:21
S32	14742	c07c2521/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:22
S33	38	S25 and S28	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:23
S34	2	S20 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	OFF	2019/07/31 14:24

			IBM_TDB			
S35	5	S28 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:25
S36	0	S25 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S37	0	S33 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S38	1	"7385092".pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 16:49
S39	1	"20170360035".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/08/01 10:10
S40	13	(biodiene? or (bio adj diene?) or (bio adj alkene) or bioalkene)	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/08/01 10:27
S41	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:13
S42	27	S41 and hydrolysis	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:13
S43	9195	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:16
S44	886	S43 and hydrolysis	USPAT	OR	OFF	2019/08/01 11:16
S45	24	S43 and hydrolysis and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:17
S46	5	S43 and (hydroxide with hydrolysis) and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:24

EAST Search History (Interference)

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Bibliographic data: JP2008007463 (A) — 2008-01-17

METHOD FOR PRODUCING 1,2-ALKANEDIOL

Page bookmark	JP2008007463 (A) - METHOD FOR PRODUCING 1,2-ALKANEDIOL
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Application number:	JP20060179791 20060629 Global Dossier
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Abstract of JP2008007463 (A)

PROBLEM TO BE SOLVED: To provide a method by which a low odor 1,2-alkanediol can readily and safely be produced in high purity. ;SOLUTION: The method for producing the 1,2-alkanediol is characterized as follows. An olefin is reacted with hydrogen peroxide in the presence of formic acid and the resultant reaction mixture is reacted with an alcohol. ;COPYRIGHT: (C)2008,JPO&INPIT

DESCRIPTION JP2008007463

An object of the present invention is to provide a method for easily and safely producing low odor 1,2-alkanediol with high purity. A method for producing 1,2-alkanediol, which comprises reacting an olefin with hydrogen peroxide in the presence of formic acid, and reacting the obtained reaction mixture with an alcohol. 【Selection chart】 None

Process for producing 1,2-alkanediol

[0001]

The present invention relates to a process for the preparation of 1,2-alkanediols. More particularly, it relates to a process for producing 1,2-alkanediols useful as raw materials for lubricating oils, cosmetics, perfumes, pharmaceuticals and the like.

[0002]

As a method for producing 1,2-alkanediol, a method is known in which an olefin is reacted with hydrogen peroxide in the presence of formic acid or acetic acid to

hydrolyze an epoxide produced (for example, Non-Patent Document 1 and 2). However, this method is disadvantageous in terms of production efficiency because it requires multiple steps of operation such as removal of the solvent, reaction with aqueous sodium hydroxide solution, and neutralization with hydrochloric acid after completion of the reaction.

[0003]

Further, as a method for producing 1,2-diol, there is known a method for producing 1,2-diol from an olefin via an epoxide, using peracetic acid as an oxidizing agent (see, for example, Patent Document 1). However, this method has the disadvantage that by-products of epoxide and diol are generated.

[0004]

On the other hand, as a method for producing 1,2-diol which can avoid the formation of by-products of epoxide and diol, hydrogen peroxide water is reacted with olefin in the presence of tungsten complex as a catalyst to produce 1,2-diol. Methods for producing diols are known (see, for example, non-patent documents 3 to 5). However, this method has the disadvantage that by-produced ketone and carboxylic acid, since the generated diol is further oxidized.

[0005]

There is also proposed a method of enhancing the selectivity of 1,2-diol by devising reaction conditions (see, for example, Patent Document 2 and Non-Patent Document 6). However, this method has a disadvantage in safety in the working environment because it uses highly toxic benzene as a solvent, and it is further extracted with a 30% aqueous sulfuric acid solution to neutralize the product and neutralized with a base There is a disadvantage in terms of manufacturing efficiency because it requires complicated operations.

[0006]

Also, as another method for producing 1,2-diol, a method is proposed in which an olefin and hydrogen peroxide water are reacted using a solid catalyst that can be easily separated by filtration (for example, non-patent literature 7-9). However, although this method has an improvement in the reaction operation, it has a disadvantage that the yield and selectivity of 1,2-diol are low because a large amount of epoxide and ketone are generated together with the target compound.

[0007]

Another method for producing 1,2-diols is a method for producing 1,2-diols, which comprises reacting olefins with hydrogen peroxide in the presence of a polymer compound having a sulfonic acid group. Has been proposed (see, for example, Patent Document 3). However, this method has disadvantages in terms of efficiency and safety, including reaction time.

[0008]

In addition, many conventional 1,2-alkanediols have a strong odor due to the inclusion of a trace amount of impurities, etc. Therefore, as 1,2-alkanediols used as raw materials for applications such as perfumes and cosmetics, etc. Is required to have a low odor.

[0009]

Patent Document 1: JP-A-4-41449 Patent Document 2: European Patent No. 146374 Patent Document 2: JP-A-2003-212804 Organic Syntheses, Coll.
3, 217-219 (1955) Journal of the American Chemical Society (J. Am. Chem. Soc. 67, pp. 1786-1788 (1945) Journal of Chemical Society (J. Chem. Soc. 2988-3000 (1949) Journal of American Oil Chemical Society (J. Am. Oil Chem. Soc. 44, pp. 316-320 (1967) Tetrahedron Lett. 29, pp. 823-826 (1988) Synthesis, pp. 295-297 (1989) Journal of the Catalysts (J. Cat.) 145, pp. 151-158 (1994) Chemical Communications (Chem. Commun. Pp. 325-326 (1998) J. Cat. 189, 40-51 (2000)

[0010]

The present invention has been made in view of the above-mentioned prior art, and an object of the present invention is to provide a method capable of easily and safely producing low odor 1,2-alkanediol with high purity.

[0011]

As a result of extensive research in view of the prior art, the present inventors reacted olefin with hydrogen peroxide in the presence of formic acid, and reacted the resulting reaction mixture with alcohol. It has been found that the 1,2-alkanediol is easily obtained in high purity, and the obtained 1,2-alkanediol exerts a surprising effect that hardly any odor is generated.

[0012]

The present invention has been completed based on such findings, and is characterized in that an olefin and hydrogen peroxide are reacted in the presence of formic acid, and the resulting reaction mixture is reacted with an alcohol. The present invention relates to a process for producing 2-alkanediol.

[0013]

According to the production method of the present invention, an effect is exhibited that low odor 1,2-alkanediol can be easily and safely produced with high purity.

[0014]

In the present invention, first, olefin and hydrogen peroxide are reacted in the presence of formic acid.

[0015]

As the olefin, various ones can be used in a wide range.
As a typical olefin, for example, formula (I): R <1> R <2> C = CR <3> R <4> (I) (wherein R <1>, R <2>, R <3> and R <4> each independently represent a hydrogen atom, an alkyl group which may have a substituent or an aryl group which may have a

substituent, and R <1>, And R & lt; 2 & gt ;, R & lt; 3 & gt ;, and R & lt; 4 & gt; together may form a ring). Two or more types can be mixed and used.

[0016]

As an alkyl group, a C1-C35 alkyl group is preferable and a C1-C21 alkyl group is more preferable.

As a substituent which the alkyl group may have, a hydroxyl group, a C1-C22 alkoxy group, etc. are mentioned, for example.

[0017]

As an aryl group, a C6-C35 aryl group is preferable and a C6-C22 aryl group is more preferable.

As a substituent which the aryl group may have, a hydroxyl group, a phenyl group, a C1-C22 alkoxy group etc. are mentioned, for example.

[0018]

In addition, two groups of R <1>, R <2>, R <3> and R <4> may be combined to form a ring.

Examples of such rings include cycloalkyl groups having 3 to 35 carbon atoms, and these rings may form multiple rings such as fused rings and non-fused rings with other rings.

Furthermore, a residue obtained by removing a hydrogen atom from any two of R <1>, R <2>, R <3> and R <4> is a divalent atom and / or a divalent functional group. They may be combined with each other to form a ring together with the carbon atom to which they are attached, and in this case, as a divalent atom, an oxygen atom, a nitrogen atom, a sulfur atom or the like, or Examples of the divalent functional group include a silylene group, an ethylenedioxy group, an arylenedioxy group, a carbonyl group, a sulfoxide group and a sulfone group.

[0019]

Specific examples of the olefin represented by the formula (I) include 1-hexene, 2,3-dimethyl-2-butene, 2-methyl-2-pentene, 2-heptene, cyclopentene, cyclohexene, 1 - Methylcyclohexene, cyclooctene, cyclododecene, 1-undecene, 1-dodecene, 2-cyclohexen-1-ol, 1-ethyl-1-cyclopentene, cinnamic alcohol, 2-methyl-3-phenyl-2-propene- 1-ol, 4- (1-propenyl) -1,2-dimethoxybenzene and the like can be mentioned.
[0020]

Hydrogen peroxide is usually used as an aqueous solution.
The concentration of hydrogen peroxide in the aqueous hydrogen peroxide solution is not particularly limited, but is preferably 1 to 80%, and more preferably 3 to 60%.
[0021]

The amount of hydrogen peroxide is preferably equal to or less than the equivalent to the olefin double bond. Usually, when the amount of hydrogen peroxide is excessive to the olefin, it is necessary to treat the excess peroxide after the reaction, and in some cases, it is removed by washing or filtration of the treatment. A process is also required, and an odorant is generated or a side reaction product is generated by a peroxide treating agent (usually, in the case of sodium thiosulfate, etc., an odor from the sulfur source is easily generated) In the case of catalysts such as manganese oxide, there are many side reactions such as oxidation of diol, and there are many cases where odor components and impurities are easily generated due to heat generation, and safety aspects due to increased risk due to excess peroxide. Therefore, it is preferably 0.5 to 1 equivalent, more preferably 0.7 to 0.95 equivalent to the olefin double bond.
[0022]

The amount of formic acid safely causes the oxidation of the olefin under milder conditions, so that the formic acid is generated in the reaction system, and the side reaction between the epoxy compound formed as an intermediate from the olefin and the diol is suppressed. Therefore, from the viewpoint of reacting an epoxy intermediate with formic acid to open the ring, it is usually 1 to 30 equivalents, more preferably 1 to

15 equivalents, more preferably from the viewpoint of production efficiency to the olefin double bond. Preferably, it is 1 to 5 equivalents.

[0023]

The reaction of an olefin and hydrogen peroxide can be easily carried out, for example, by mixing the olefin and formic acid, and then adding hydrogen peroxide to the mixture while stirring the obtained mixture.

[0024]

The reaction temperature of the olefin and hydrogen peroxide is usually 20 to 100 ° C, preferably 30 to 60 ° C.

[0025]

A solvent may be used in the reaction of the olefin and hydrogen peroxide.
Examples of the solvent include ethers, esters, nitriles, amides, sulfoxides, hydrocarbon compounds and the like.
The amount of the solvent is not particularly limited, but generally, it is preferably 1000 parts by volume or less, more preferably 300 parts by volume or less, per 100 parts by volume of the olefin.

[0026]

The end point of the reaction between the olefin and the hydrogen peroxide can be easily confirmed by, for example, analysis by gas chromatography and confirmation of disappearance of the peracid by titration of the peroxide.

[0027]

Thus, the reaction of the olefin with hydrogen peroxide gives a reaction mixture containing the ester formed.
The resulting reaction mixture may be concentrated if necessary.

[0028]

Next, the reaction mixture obtained is reacted with an alcohol.
Such a reaction is specifically a transesterification reaction of the formed ester contained in the obtained reaction mixture with an alcohol.
[0029]

As alcohol, a C1-C4 linear or branched monohydric alcohol is mentioned, for example. Specific examples of such monohydric alcohols include methanol, ethanol, isopropanol and the like, but the present invention is not limited to such examples.
[0030]

The amount of alcohol is the total of the ester portion of the formed ester contained in the reaction mixture and the remaining formic acid, from the viewpoint of completely formicifying the ester site contained in the reaction mixture and the remaining formic acid. Preferably, it is 1 to 10 equivalents, more preferably 2 to 10 equivalents, still more preferably 3 to 5 equivalents.
[0031]

In addition, a catalyst can be used in the case of reaction with the obtained reaction mixture and alcohol.
As a catalyst, what is generally used in the case of transesterification may be used. Examples of the catalyst include sulfonyl compounds such as sulfuric acid and paratoluenesulfonic acid, acid catalysts such as polymer compounds having a sulfonic acid group, metals such as lithium compounds, titanium compounds, sodium compounds, aluminum compounds, tin compounds, zinc compounds and the like Although a catalyst etc. are mentioned, this invention is not limited only to this illustration.
[0032]

The amount of the catalyst is not particularly limited, but generally it is preferably 0.01 to 5 parts by weight, more preferably 0.05 to 1 part by weight, per 100 parts by weight of the reaction mixture.

[0033]

Moreover, although reaction of an olefin and hydrogen peroxide can also be normally performed without using a solvent, it is also possible to use a solvent.
As the solvent, those generally used in oxidation reaction and transesterification reaction can be used. Examples of the solvent include ethers, nitriles, amides, sulfoxides, hydrocarbon compounds and the like. The amount of the solvent is not particularly limited, but generally, it is preferably 50 to 1000 parts by volume, more preferably 100 to 300 parts by volume, per 100 parts by volume of the olefin.
[0034]

The reaction of the obtained reaction mixture with the alcohol can be carried out, for example, by adding and mixing an alcohol and, if necessary, a catalyst to the reaction mixture.
[0035]

The reaction temperature is preferably in the range of usually 20 to 80 ° C., and from the viewpoint of advancing the equilibrium reaction by selectively taking out the formic acid ester to be produced out of the reaction system, the boiling point or less of the alcohol used and it is more preferable that it is more than the boiling point of the formic acid ester to be produced.
During the reaction, it is preferable to recover the formic acid ester to be produced, but in particular, when methanol is used as the alcohol, methyl formate having a boiling point lower than that of other formate esters is generated, so that it is milder. The reaction of the reaction mixture with the alcohol can be carried out under the conditions, and since methanol and methyl formate do not azeotrope and only methyl formate volatilizes, methyl formate can be easily removed out of the reaction system.
[0036]

The reaction of the reaction mixture with the alcohol can usually be carried out without using a solvent, but it is also possible to use a solvent. As the solvent, those used in

transesterification can be used. Examples of the solvent include ethers, nitriles, amides, sulfoxides, hydrocarbon compounds and the like.

[0037]

The end point of the reaction of the reaction mixture with the alcohol can be easily confirmed, for example, by analysis by gas chromatography.

[0038]

Thus, the target compound 1,2-alkanediol is obtained.
When a catalyst is used in the reaction, it is preferable to neutralize the catalyst by adding an alkali to the reaction mixture containing the formed 1,2-alkanediol.

[0039]

The formate ester, formic acid and alcohol contained in the reaction mixture containing 1,2-alkanediol can be recovered by concentrating the reaction mixture and reused. The obtained 1,2-alkanediol may be purified by, for example, distillation. In addition, when the 1,2-alkanediol exhibits such a water solubility that allows at least a transition to the aqueous layer when it is mixed with water, the 1,2-alkanediol is selected from normal hexane, cyclohexane, 2- By mixing with a hydrophobic solvent such as methyl hexane and water, the odor component is transferred to the organic layer, and the 1,2-alkanediol is transferred to the aqueous layer, thereby reducing the odor and reducing the 1,2-alkanediol to water It can be extracted into layers.

[0040]

The production method of the present invention is excellent in safety in the working environment because it does not require highly toxic solvents such as benzene. Moreover, according to the production method of the present invention, 1,2-alkanediol can be easily obtained in high purity and high yield. Furthermore, since the 1,2-alkanediol obtained by the production method of the present invention hardly emits an odor, it can be suitably used as a raw material for lubricating oils, cosmetics, perfumes, pharmaceuticals and the like.

[0041]

Next, the present invention will be described in more detail based on examples, but the present invention is not limited to such examples.

[0042]

Example 1 (1) Reaction of Olefin with Hydrogen Peroxide 100 g of 1-hexene and 237.5 g of formic acid (purity 95%) are mixed in a 1 liter beaker, and the resulting mixture is heated with stirring. When reaching 30 ° C., 98.2 g of a 35% aqueous hydrogen peroxide solution was slowly added to the mixture over 10 hours.
Since the reaction exothermed, the mixture was externally cooled to a temperature of 30 to 40 ° C.

[0043]

After completion of the addition of the aqueous hydrogen peroxide solution, the reaction was terminated by maintaining the temperature of the mixture at 35 ° C. for 2 hours. The end point of the reaction was confirmed by titration of the amount of peroxide (potassium iodide titration method). The resulting reaction mixture is concentrated until the amount of excess formic acid is distilled off (there is no need to completely concentrate the formic acid because it is also a formic acid ester), and the concentrated reaction mixture is subjected to the next alcohol Used for reaction.

[0044]

(2) Reaction of reaction mixture and alcohol 176.7 g of the concentrated reaction mixture obtained in the above (1), 170 g of methanol and 0.09 g of p-toluenesulfonic acid monohydrate are mixed in a 1 liter beaker The resulting methyl formate was stirred at 55 ° C. for 7 hours while being removed from the beaker. Thereafter, 0.08 g of a 30% aqueous solution of sodium hydroxide is added to the beaker to neutralize the catalyst (p-toluenesulfonic acid monohydrate), and then methanol is distilled off under reduced pressure to obtain 1,2- 120.7 g of hexanediol was obtained. As a result, the yield of 1,2-hexanediol was 92%, and the purity of 1,2-hexanediol was 92%.

[0045]

Next, when the obtained 1,2-hexanediol is purified by distillation, the yield is 76%, and by further re-distilling the initial distillation, the purity is 98% or more with a distillation yield of 94% 1, 2-Hexanediol was obtained.

[0046]

Example 2 1, 2-Hexanediol was prepared as in Example 1 and was purified to distillation.

5 g (purity 98%) of the obtained 1,2-hexanediol, 10 g of normal hexane and 10 g of water were mixed and stirred at 25 ° C. Separate the hexane layer and concentrate the aqueous layer to remove the odor component, 4.9 g of 1,2-hexanediol (98% yield, relative to 1,2-hexanediol mixed with normal hexane and water, purity 99 %) Got.

[0047]

Examples 3 to 9 In the same manner as in Example 1, except that olefins shown in Table 1 were used instead of 1-hexene and formic acid, hydrogen peroxide aqueous solution etc. were used in the amounts shown in Table 1, An alkanediol is obtained. The obtained 1,2-alkanediol and its yield and purity are shown in Table 1.

[0048]

[0049]

Comparative Example 1 41 g of cyclohexene is charged into a glass flask and heated to 30 ° C. while stirring.

When 30 ° C. was reached, 30% peracetic acid was slowly added over a period of 2 hours to a molar ratio of 1.2 times. Since the reaction is exothermic, the mixture was cooled from the outside so that the temperature of the mixture became about 30 ° C. After completion of the peracetic acid addition, the reaction was completed by maintaining the temperature of the mixture at 30 ° C. for 1 hour. The reaction crude

solution was analyzed by gas chromatography to confirm that cyclohexene oxide was obtained in 93% of the yield.

[0050]

50 g of water was charged into a glass flask and heated with stirring, and when reaching 70 ° C., 21.6 g of the solution containing cyclohexene oxide obtained above and acetic acid was slowly added over 2 hours. After completion of the addition of the solution, the reaction crude solution was immediately analyzed by gas chromatography. As a result, cyclohexane-1,2-diol was obtained in 94% yield based on cyclohexene oxide and 87.4% based on cyclohexene It confirmed that it was obtained by the yield.

[0051]

Comparative Example 2 500 mg of Nafion-NR50 (manufactured by DuPont) (equivalent weight of sulfonic acid group to olefin is equivalent to 0.04), 2.23 g (19.6 mmol) of a 30% aqueous hydrogen peroxide solution and 825 mg of 1-hexene (9. 81 mmol) were mixed and stirred at 70 ° C. for 24 hours. As a result of analyzing the reaction solution by gas chromatography, almost no progress of the reaction was observed.

[0052]

The reaction solution was filtered to remove Nafion-NR50, and 10 mg (0.115 mmol) of manganese dioxide was added to decompose excess hydrogen peroxide present in the solution. The reaction solution was filtered and then water and the like were distilled off using a rotary evaporator to obtain 1,2-hexanediol as a concentrated mixture (yield: less than 5%).

[0053]

Comparative Example 3 In 176.7 g of the concentrated reaction mixture obtained in the same manner as the reaction of (1) olefin and hydrogen peroxide in Example 1, 239.3 g of a 30% aqueous solution of sodium hydroxide was added to 20 to 35 It dripped at ° C. The end point of the reaction was confirmed by analysis by gas chromatography. To the obtained reaction mixture, 142.4 g of methyl tertiary butyl ether as an extraction solvent

was added, and after stirring, the mixture was allowed to stand to separate an aqueous layer containing potassium formate. To the organic layer, 71.2 g of 20% brine was added and washed, and after stirring and standing, the aqueous layer was separated. After the washing operation was performed a total of three times, the organic layer was concentrated to remove methyl tertiary butyl ether to obtain 118.1 g of 1,2-hexanediol. As a result, the yield of 1,2-hexanediol was 85.2%, and the purity of 1,2-hexanediol was 85%. Moreover, the odor derived from a solvent and the odor by strong alkali treatment were seen by this 1, 2- hexanediol.

[0054]

Experimental Example The 1,2-alkanediols obtained in Examples 1 to 9 and Comparative Examples 1 and 3 and a 5 wt% 1,2-alkanediol aqueous solution obtained by diluting them with purified water 20 times were prepared.

[0055]

In a 100 mL glass jar, put the above-prepared 1,2-alkanediol or 5% by weight 1,2-alkanediol aqueous solution, and randomly extracted each panel of 20 men and women by using a bottle neck. The odor was confirmed, and each of the 1,2-alkanediol and the 5 wt% 1,2-alkanediol aqueous solution was evaluated based on the following evaluation criteria.

The results are shown in Table 2. The 1,2-alkanediol itself obtained in Examples and Comparative Examples is an odorless compound.

[0056]

[Evaluation Criteria] ○: Almost odorless. :: Slightly smelly. X: The odor is clearly felt.

[0057]

Next, based on the above results, the number of persons who performed each evaluation was counted, and ranking was performed according to the following criteria. In addition, the rank of S or more is a pass.

[0058]

[Rank] SSS: When there are 18 or more evaluators who have evaluated ○ SS: There are 15 to 17 evaluators who have evaluated ○, and there is no one who has evaluated × S: When there are 15 to 17 evaluators who have a rating of ○ and there are evaluators who have a rating of A A: When there are 10 to 14 evaluators who have a rating of B B: Evaluation that has a rating of ○ When there are 5 to 9 persons C: If there are 4 or less evaluators who have made an evaluation

[0059]

[0060]

From the results shown in Table 1, according to the methods of Examples 1 to 9, the odor of the produced 1,2-alkanediol is relatively unlikely to be generated, even in comparison with the conventional Comparative Examples 1 and 3. It can be seen that the odor of 1,2-hexanediol can be reduced.

[0061]

Further, according to Examples 1 to 9, since a solvent such as highly toxic benzene is not required, the safety in the working environment is excellent, and the sodium thiosulfate and manganese of the peroxide conventionally required are required. There is no need for operations such as treatment with peracid including catalyst or treatment with strong alkali of ester, and the oxidation reaction can be performed at a temperature lower than conventional, so the odor is reduced 1,2-alkane It can be seen that diols can be produced easily and efficiently safely.

[0062]

Therefore, it is understood that according to the production method of the present invention, 1,2-alkanediol useful as a raw material for lubricating oil, cosmetics, perfumes, pharmaceuticals and the like can be easily and safely produced with high purity.

[0063]

The 1,2-alkanediol obtained by the production method of the present invention can be suitably used as a raw material for lubricating oils, cosmetics, perfumes, pharmaceuticals and the like.

CLAIMS JP2008007463

1.

1. A process for producing 1,2-alkanediol, which comprises reacting an olefin with hydrogen peroxide in the presence of formic acid, and reacting the resulting reaction mixture with an alcohol.

2.

The olefin is represented by the formula: R <1> R <2> C = CR <3> R <4> (I) (wherein R <1>, R <2>, R <3> and R <4> are And each independently represents a hydrogen atom, an alkyl group which may have a substituent, or an aryl group which may have a substituent, and R <1>, R <2>, R <3> And R <4> may form a ring together) and an olefin represented by the formula:

3.

The method according to claim 1 or 2, wherein the amount of hydrogen peroxide is 0.5 to 1 equivalent based on the olefin double bond.

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1

CONFIRMATION NO. 3410

159443
Calderone Bullock LLC
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PUBLICATION NOTICE

OC000000110263056

Title: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

Publication No.US-2019-0241491-A1
Publication Date:08/08/2019

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

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Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

PTO/SB/06 (09-11)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 16/262,898	Filing Date 01/30/2019	☐ To be Mailed

ENTITY: ☑ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $100 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $460 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	02/06/2020	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 38	Minus	** 41	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 0		x $460 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/MARSHA R RICHARDS/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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In Re Patent Application of: Inolex Investment Corporation			
Conf. No.:	3410	Group Art Unit:	1622
Appln. No.:	16/262,898	Examiner:	Yate Kai Rene Cutliff
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Process for Making the Same		

AMENDMENT

This is in response to the Office Action dated August 6, 2019 (Paper No. 20190801). This response is being timely submitted by February 6, 2020 in view of the simultaneous submission of a three-month Petition for Extension of Time, including authorization to charge the appropriate fee.

Please amend the above-identified application, without prejudice, as follows:

Amendments to and Listing of the Claims:

Please cancel claims 35-41, without prejudice to the filing of one or more related applications; amend claim 12 without prejudice; add new claims so that the claims read as follows with the changes as shown:

1. (original) A process for the synthesis of bio-1,2-alkanediols, comprising:

providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and

converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

2. (original) The process of claim 1, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain of about 6 to about 14 carbon atoms.

3. (original) The process according to claim 2, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain length of about 6 to about 10 carbon atoms.

4. (original) The process according to claim 3, wherein the bio-alkene and the bio-1,2-alkanediol each have a carbon chain length of about 6 to about 8 carbon atoms.

5. (original) The process according to claim 1, wherein the bio-alkene is bio-octene and the bio-1,2-alkane diol is bio-1,2-octanediol.

6. (original) The process according to claim 1, wherein the bio-alkene results from a process wherein a bio-1-alcohol is dehydrated by heating the bio-1-alcohol in a reactor with a catalyst.

7. (original) The process according to claim 6, wherein the reactor is a fixed bed reactor.

8. (original) The process according to claim 7, wherein the fixed bed reactor is a fluidized fixed bed reactor.

9. (original) The process according to claim 6, wherein the catalyst is selected from $ZnAl_2O_4$ and a γ-alumina catalyst.

10. (original) The process according to claim 9, wherein the bio-alkene has a bio-1-alkene regioselectivity of about 92% to about 99%.

11. (original) The process according to claim 10, wherein the bio-alkene have a bio-1-alkene regioselectivity of about 95% to about 99%.

12. (currently amended) The process according to claim ~~1~~ 11, wherein the process yields at least about 92% to about 99% of the bio-1,2-alkanediol.

13. (original) The process according to claim 9, wherein the catalyst is a γ-alumina catalyst is treated with a base to form a modified γ-alumina catalyst.

14. (original) The process according to claim 13, wherein the base comprises a Group I or a Group II metal.

15. (original) The process according to claim 9, wherein the γ-alumina catalyst is treated with a calcium promoter to provide a modified γ-alumina catalyst.

16. (original) The process according to claim 15, wherein the modified γ-alumina catalyst is calcined to provide a calcined γ-alumina catalyst.

17. (original) The process according to claim 16, wherein the calcium promoter is used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination.

18. (original) The process according to claim 17, wherein the calcium promoter is used in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination.

19. (original) The process according to claim 15 wherein a temperature during calcination is about 400°C to about 500°C.

20. (original) The process according to claim 19, wherein the temperature during calcination is about 420°C to about 480°C.

21. (original) The process according to claim 20, wherein the temperature during calcination is about 440°C to about 460°C.

22. (original) The process according to claim 15, wherein calcination is carried out in an oven.

23. (original) The process according to claim 15, wherein the calcination is carried out in an atmosphere of air or inert gas.

24. (original) The process according to claim 6, wherein the bio-alkene undergoes a distillation step to refine the bio-alkene prior to converting the bio-alkene to the bio-1,2-alkanediol.

25. (original) The process according to claim 6, wherein the bio-1,2-alkanediol formed from the bio-alkene undergoes a final distillation step to refine the bio-1,2-alkanediol.

26. (original) The process according to claim 1, wherein the bio-alkene results from a process wherein the bio-1-alcohol in water is dehydrated by heating the bio-1-alcohol with a catalyst under a purge gas.

27. (original) The process according to claim 1, wherein the bio-alkene is converted to the bio-1,2-alkanediol by reacting the bio-alkene in the presence of at least one of formic acid or acetic acid and a peroxide to form a bio-1,2-epoxyalkane having an epoxy ring, and contacting the 1,2-epoxyalkane with water and sodium hydroxide to form the bio-1,2-alkanediol.

28. (original) The process according to claim 1, wherein the process yields at least about 60% to about 99% of the bio-1,2-alkanediol.

29. (original) The process according to claim 28, wherein the process yields at least about 72% to about 99% of the bio-1,2-alkanediol.

30. (original) A process for making bio-1,2-alkanediols, comprising:

providing a bio-1-alcohol and a catalyst treated with a base;

dehydrating the bio-1-alcohol in the presence of the catalyst to form a bioalkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and

converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms.

31. (original) The process according to claim 30, wherein the catalyst is a γ-alumina catalyst and the base comprises calcium.

32. (original) The process according to claim 31, wherein the γ-alumina catalyst is treated with a calcium promotor and after treatment is calcined at a temperature of about 400°C to about 500°C.

33. (original) The process according to claim 30, wherein the process yields about 72% to about 99% of the bio-1,2-alkanediol.

34. (original) The process according to claim 30, wherein the bio-1-alkene regioselectivity is about 95% to about 99%.

35-87. (canceled).

88. (new) The process of claim 1, wherein the bio-alkene is converted to the bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms by reacting the bio-

alkene in the presence of at least one of a peracid and a hydroxide to form a reaction product, and contacting the reaction product with water and a base to form the bio-1,2-alkanediol.

89. (new) The process according to claim 88, wherein the bio-alkene is converted to the bio-1,2-alkanediol by reacting the bio-alkene in the presence of at least one of formic acid or acetic acid and a peroxide to form a bio-1,2-epoxyalkane having an epoxy ring, and contacting the 1,2-epoxyalkane with water and sodium hydroxide to form the bio-1,2-alkanediol.

90. (new) The process according to claim 30, wherein the bio-alkene is converted to the bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms by reacting the bio-alkene in the presence of at least one of a peracid and a hydroxide to form a reaction product, and contacting the reaction product with water and a base to form the bio-1,2-alkanediol.

91. (new) The process according to claim 90, wherein the bio-alkene is converted to the bio-1,2-alkanediol by reacting the bio-alkene in the presence of at least one of formic acid or acetic acid and a peroxide to form a bio-1,2-epoxyalkane having an epoxy ring, and contacting the 1,2-epoxyalkane with water and sodium hydroxide to form the bio-1,2-alkanediol.

REMARKS

Claims 1-34 and 88-91 are pending in the application.

Claim 12 has been amended to correct its dependency. Claims 35-41 have been canceled without prejudice to the filing of one or more related applications. New claims 88-91 have been added. The amendment to claim 12 is supported in the original claims and in the specification, at least, at paragraph [0033]. The new claims are supported by the original claims as filed and also by the specification, at least, at paragraphs [0012], [0038], [0090] and [0093]. No new matter has been added by these amendments.

Objection to Claim 40

The Examiner has objected to claim 40 for omitting a word(s) before "temperature." Applicant has canceled claims 40 without prejudice so that this rejection is now moot.

Rejection of Claims 1-34 and 39-41 Under Section 112, Second Paragraph and Indefinite

The Examiner has rejected claims 1-34 and 39-41 as indefinite for not distinctly claiming the subject matter which the applicant regards as his invention.

Specifically, the Examiner argues that the process claims omit an "essential step" relating to conversion of a bio-alkene to a bio-1,2-alkanediol. The Examiner points to an Example 7 and to the disclosure's description of a preferred chemical pathway to convert the bio-alkene to a bio-1,2-alkanediol. The Examiner acknowledges that the applicant's disclosure teaches that various known chemical reactions can be used for this purposes such as those used to convert petrochemically-derived alkenes to their resulting petrochemically derived alkanediols, but then reasons that the disclosure follows specific process steps to achieve the complete formation of the 1,2-alkanediol. The Examiner further cites prior art patents that require treatment after an initial reaction to form an alkanediol.

To be indefinite, the claim must be such that "... a person of ordinary skill in the art would understand the scope of the claim term ... with reasonable certainty." See, *Eli Lilly and Company v. Teva Parenteral Medicines, Inc.*, 845 F.3d 1357 (Fed. Cir. 2017). In this instance, the specification provides guidance that a 1,2-alkanediol may be made by various conversion pathways from a starting material in the form of an alkene. In the prior art, such starting materials were petrochemically derived and there was insufficient regioselectivity in the alkenes available using standard chemical pathways to achieve a high yield of the 1,2-alkanediol species

among those diols formed. *See*, Specification, at page 6-7, paragraphs [0019]-[0021], wherein the applicant describes that prior art alkene starting reactants were formed from petrochemically derived alcohols, which were isomeric mixtures, such that when converted to an alkanediol, the resulting end products formed isomers in a manner that provided low yields of the desired 1,2-alkanediol product.

Thus, the applicant's invention which is of significant benefit particularly in the personal care arts provides the claimed bio-alkene, having a high regioselectivity, that upon its conversion to the resulting bio-1,2-alkanediols provides that species in a high yield. The chemical pathway to convert the alkene to the alkane may be carried out by any known chemical pathway for this purpose (See, specification at paragraph [0092]), whether by a single step or multiple steps and which can use various conversion techniques known in the art of alkene to alkanediol conversion used with petrochemically-derived alkenes. *See*, specification, at paragraph [0089]-[0092]. While exemplary pathways are provided in the specification, the specific pathway for conversion of the unique bio-alkene starting materials of high regioselectivity need not occur in a particular manner so long as the bio-alkenes as claimed are processed chemically to result in the bio-1,2-alkanediols.

One skilled in the art at the time of the invention would appreciate that the applicant's invention as claimed is focused on providing a process that uses a unique starting material that allows for formation of a unique end product upon chemical conversion. Thus, the invention would be reasonably understood by those skilled in the art at the time of the invention.

The Examiner's comments that "specific process steps are needed for the 1,2 alkanediol to be completely formed," presume that the word "converting" in the claims is a one-step reaction and/or that the specific reactions exemplified are necessary. While an Examiner may use the broadest reasonable interpretation of claim language in examination, such interpretation may not be inconsistent with the specification and file history which is relevant to evaluating indefiniteness. The Examiner's interpretation is not consistent with the specification's description of a "conversion" that is a two-step conversion and that is equated with prior art conversions that may or may not be the same conversion. The specification explains that the importance is the starting bio-alkene of high regioselectivity that allows for a more high-yield of end product 1,2-alkanediol after conversion.

Based on the foregoing, the Examiner's read of the claims is inconsistent with the file history, and one skilled in the art would readily and reasonably understand the scope of the claims based on the disclosure. Therefore, applicant respectfully requests withdrawal of this rejection.

Section Rejection of Claims 39-41 as Indefinite

The Examiner rejected claim 39-41 as lacking sufficient antecedent basis. These claims have been deleted, such that this rejection is now moot.

Section 103 Rejection of Claims 35-41

The Examiner rejected claims 35-41 as unpatentable under 35 U.S.C.§103 based on U.S. Patent Publication No. WO 2016/007196 A1 of Wright *et al.* ("Wright"). Applicant respectfully traverses this rejection, but in view of the cancelation of claims 35-41, the rejection is currently moot. Applicant reserves its right to traverse this rejection (and any other mooted rejection herein) in any related application filing re-introducing the canceled claims.

Conclusion

In view of the foregoing, applicant submits that the pending claims comply with §112 over the reasons cited by the Examiner. Withdrawal of the rejections and a Notice of Allowance are respectfully requested.

Respectfully submitted,

INOLEX INVESTMENT CORPORATION

2/4/20 By: _____
(Date)

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LLC:llc
Enclosures: Petition for Extension of Time

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Patent Application of: Inolex Investment Corporation			
Conf. No.:	3410	Group Art Unit:	1622
Appln. No.:	16/262,898	Examiner:	Yate Kai Rene Cutliff
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Process for Making the Same		

PETITION FOR EXTENSION OF TIME UNDER (37 C.F.R. § 1.136(a))

Applicant in the above-identified application hereby petitions for a three-month extension of time to and including February 6, 2020 for responding to the Office Action of August 6, 2019. A Response to Office Action is being filed simultaneously with the filing of this Petition.

[X] Applicant herewith charges the required fee under 37 C.F.R. §1.136(a) in the amount of $1400 to credit card account, Calderone Bullock American Express (Billing No. I0113.0249). **[X]** The Commissioner is hereby authorized to charge or credit as appropriate Deposit Account No. 60-2689 (Billing No. I0113.0249) for: [ ] The required fee in the amount of $__; **[X]** Any deficiencies or overpayments in the above-calculated fee.

Respectfully submitted,

INOLEX INVESTMENT CORPORATION

2/6/20 By: _____
(Date)

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LLC:llc

Electronic Patent Application Fee Transmittal

Application Number:	16262898
Filing Date:	30-Jan-2019
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	lynda Leigh Calderone
Attorney Docket Number:	I0113-198U1

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension - 3 months with $0 paid	1253	1	1400	1400
Miscellaneous:				
			Total in USD ($)	**1400**

Electronic Acknowledgement Receipt

EFS ID:	38520098
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	159443
Filer:	lynda Leigh Calderone
Filer Authorized By:	
Attorney Docket Number:	I0113-198U1
Receipt Date:	06-FEB-2020
Filing Date:	30-JAN-2019
Time Stamp:	23:34:43
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1400
RAM confirmation Number	E202026N35107034
Deposit Account	602689
Authorized User	Lynda Calderone

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		amendl0113.pdf	397734 7fdbbfb7b6bd0ba4305102d27b82a894103e9e5b	yes	8

Multipart Description/PDF files in .zip description		
Document Description	**Start**	**End**
Amendment/Req. Reconsideration-After Non-Final Reject	1	1
Claims	2	5
Applicant Arguments/Remarks Made in an Amendment	6	8

Warnings:					
Information:					
2	Extension of Time	eotl0113.pdf	53682 e9dc676dd9acece3ce2def150c9fb016175b191e	no	1
Warnings:					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	30858 7c7492b7fb4d79d934e56df865bce8160d7cc327	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	482274		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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NOTICE OF ALLOWANCE AND FEE(S) DUE

159443 7590 04/13/2020

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EXAMINER
CUTLIFF, YATE KAI RENE

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 04/13/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	07/13/2020

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

159443 7590 04/13/2020

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	07/13/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑ Issue Fee ❑ Publication Fee (if required) ❑ Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

159443 7590 04/13/2020

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

EXAMINER	
CUTLIFF, YATE KAI RENE	
ART UNIT	**PAPER NUMBER**
1622	

DATE MAILED: 04/13/2020

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/262,898	Applicant(s) Burgo et al.	
	Examiner YATE K CUTLIFF	Art Unit 1622	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to 2/6/2020.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-34 and 88-91 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Response to Amendment

2. The amendment to claim 12 and new claims 88 - 91, submitted February 6, 2020 is acknowledged and entered.

Response to Arguments

3. Applicant's arguments, see page 6, filed February 6, 2020, with respect to the objection of claim 40 have been fully considered and are persuasive in view of the cancellation of claim 40. The objection of claim 40 has been withdrawn.

4. Applicant's arguments, see pages 6 - 8, filed February 6, 2020, with respect to the rejection of claims 1 – 34 and 39 – 41 under 35 USC 112(b) have been fully considered and are persuasive in view of the arguments presented and cancellation of claims 39 - 41. The rejection of claims 1 – 34 and 39 – 41 under 35 USC 112(b) has been withdrawn.

5. Applicant's arguments, see page 8, filed February 6, 2020, with respect to the rejection of claims 35 – 41 under 35 USC 103 have been fully considered and are persuasive in view of the cancellation of claims 35 - 41. The rejection of claims 35 – 41 under 35 USC 103 has been withdrawn.

Allowable Subject Matter

6. Claims 1- 34 and 88 – 91 are allowed.

7. The following is an examiner's statement of reasons for allowance: the Examiner has considered the amendment filed by the Applicant on February 6, 2020 and the arguments therein. Applicant's arguments were found persuasive; as such, the Examiner has withdrawn the rejections made in the previous Office Action. Accordingly, the instant claims are now allowed.

8. Osterholt et al. (US 7,385,092), discloses a process for the synthesis of 1.2-alkanediols (a process for synthesis of 1,2-hexanediol or 1,2-octanediol; column 10 ln 46 to column 11 ln 35), comprising: providing an alkene having a carbon chain of about 5 to about 20 carbon atoms; and converting the alkene to a 1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms (providing 1-hexene and converting it into 1,2-hexanediol, or providing 1-octene and converting it to 1.2-octanediol; column 10 ln 46 to column 11 ln 35). In Osterholt, in a reaction of 1-alkene, the intermediates are subjected to acid catalyzed transesterification without additional base hydrolysis to obtain the final 1,2-alkanediol. While Osterholt discloses chemical synthesis of 1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms by conversion of alkene (Osterholt; column 10 ln 46 to column 11 ln 35), Osterholt **fails** to disclose a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms synthesized by conversion of a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably

accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

9. Any inquiry concerning this communication or earlier communications from the examiner should be directed to YATE K. CUTLIFF whose telephone number is (571)272-9067. The examiner can normally be reached on Monday-Friday (8:30 - 5:30).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf can be reached on (571) 272 - 2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020							
	1	✓	=							
	2	✓	=							
	3	✓	=							
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	40	✓	-							
	41	✓	-							
	42		-							

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020							
	43		-							
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	45		-							
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	91		=							

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CPC								
Symbol							**Type**	**Version**
C07C	/	29	/	04			F	2013-01-01
C07C	/	31	/	20			I	2013-01-01
C07C	/	29	/	80			I	2013-01-01
B01J	/	23	/	06			I	2013-01-01
B01J	/	37	/	08			I	2013-01-01
B01J	/	21	/	04			I	2013-01-01
A01N	/	31	/	02			I	2013-01-01
A61K	/	8	/	345			I	2013-01-01
A61Q	/	19	/	00			I	2013-01-01
C11D	/	3	/	2044			I	2013-01-01
C11D	/	3	/	48			I	2013-01-01
C07C	/	1	/	24			I	2013-01-01
C07C	/	29	/	48			I	2013-01-01
C07C	/	11	/	02			I	2013-01-01
C07C	/	11	/	107			I	2013-01-01
B01J	/	2523	/	27			A	2013-01-01
C07B	/	41	/	02			A	2013-01-01
C07B	/	63	/	00			A	2013-01-01
B01J	/	2523	/	31			A	2013-01-01
A61L	/	2	/	18			A	2013-01-01
A61Q	/	5	/	00			A	2013-01-01
A61Q	/	11	/	00			A	2013-01-01
C07C	/	2521	/	04			A	2013-01-01

CPC Combination Sets									
Symbol							**Type**	**Set**	**Ranking**	**Version**
C07C	/	1	/	24			I	1	1	2013-01-01
C07C	/	11	/	02			I	1	2	2013-01-01
C07C	/	29	/	48			I	2	1	2013-01-01
C07C	/	31	/	20			I	2	2	2013-01-01

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	03 April 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20200403

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CPC Combination Sets								
Symbol					**Type**	**Set**	**Ranking**	**Version**
C07C	/	29	/	80	I	3	1	2013-01-01
C07C	/	31	/	20	I	3	2	2013-01-01

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	03 April 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

INTERNATIONAL CLASSIFICATION					
CLAIMED					
C07C	/	29	/	04	
C07C	/	29	/	48	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	03 April 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	13	13	25	25		37		49		61		73		85
2	2	14	14	26	26		38		50		62		74		86
3	3	15	15	27	27		39		51		63		75		87
4	4	16	16	28	28		40		52		64		76	35	88
5	5	17	17	29	29		41		53		65		77	36	89
6	6	18	18	30	30		42		54		66		78	37	90
7	7	19	19	31	31		43		55		67		79	38	91
8	8	20	20	32	32		44		56		68		80		
9	9	21	21	33	33		45		57		69		81		
10	10	22	22	34	34		46		58		70		82		
11	11	23	23		35		47		59		71		83		
12	12	24	24		36		48		60		72		84		

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	03 April 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC - Searched*		
Symbol	Date	Examiner
C07C 29/04, 48	04/03/2020	ykc
C07C 31/20	04/03/2020	ykc
C07C 33/025	08/01/2019	ykc
C07C 2521/04	04/03/2020	ykc
B01J 21/04	04/03/2020	ykc
B01J 23/06	08/01/2019	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	04/03/2020	ykc
C07B 41/02	04/03/2020	ykc

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

U.S. Patent and Trademark Office

Part of Paper No.: 20200403

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

Search Notes		
Search Notes	**Date**	**Examiner**
Palm Inventor Search	04/03/2020	ykc
East	04/03/2020	ykc
C07C 29/04, 48	04/03/2020	ykc
C07C 31/20	08/01/2019	ykc
C07C 33/025	08/01/2019	ykc
C07C 2521/04	04/03/2020	ykc
B01J 21/04	04/03/2020	ykc
B01J 23/06	08/01/2019	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	04/03/2020	ykc
C07B 41/02	04/03/2020	ykc

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
C07C	29/04, 48	04/03/2020	ykc
C07C	31/20	04/03/2020	ykc
C07C	2521/04	04/03/2020	ykc
B01J	21/04	04/03/2020	ykc
C07C	11/02, 107	04/03/2020	ykc
C07B	41/02	04/03/2020	ykc

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:57
S2	69	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S3	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S4	69	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S5	2	"2016007196".pn.	US-PGPUB; USPAT; USOCR; FPRS; EPO	OR	OFF	2019/07/31 11:33
S6	9189	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:43
S7	1392	(natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:45
S8	23	S6 and S7 and alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 12:46
S9	9170	(method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S10	684	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and dehydration	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S11	378	S10 and (natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:51
S12	125	S11 and (alkene or octene or pentene	US-PGPUB;	OR	OFF	2019/07/31

		or hexene or heptene or nonene or decene or dodecene)	USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB			13:02
S13	125	S12 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:03
S14	9170	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S15	1219	S14 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:05
S16	1175	S15 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S17	55	S14 and (terminal with (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:07
S18	3	("20050006997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:29
S19	3	("20050069997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:30
S20	5912	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:35
S21	2221	S20 and (natural or plant or vegetable or ferment$4 or biomass)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:40
S22	312	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and (peracid or formic of acetic) and (hydrogen adj peroxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S23	308	S22 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S24	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:51

		acetic) with (hydrogen adj peroxide))				
S25	3031	C07C29/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:15
S26	5809	C07C31/20.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S27	0	C07C33/25.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S28	3127	C07C33/025.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S29	18997	B01J21/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S30	16230	B01J37/08.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:18
S31	4501	B01J23/06.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:21
S32	14742	c07c2521/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:22
S33	38	S25 and S28	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:23
S34	2	S20 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT;	OR	OFF	2019/07/31 14:24

			IBM_TDB			
S35	5	S28 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:25
S36	0	S25 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S37	0	S33 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S38	1	"7385092".pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 16:49
S39	1	"20170360035".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/08/01 10:10
S40	13	(biodiene? or (bio adj diene?) or (bio adj alkene) or bioalkene)	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/08/01 10:27
S41	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:13
S42	27	S41 and hydrolysis	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:13
S43	9195	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:16
S44	886	S43 and hydrolysis	USPAT	OR	OFF	2019/08/01 11:16
S45	24	S43 and hydrolysis and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:17
S46	5	S43 and (hydroxide with hydrolysis) and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:24

S47	1	"20140066666".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:26
S48	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:29
S49	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:30
S50	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S51	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S52	2015	c07c29/48.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:49
S53	1075	c07b41/02.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:54
S54	24629	c07c11/02,107.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S55	32	S53 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S56	9	S55 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S57	23	S52 and S53	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S58	5	S57 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S59	48	S52 and S54	US-PGPUB; USPAT; USOCR; FPRS;	OR	OFF	2020/04/03 12:58

			EPO; JPO; DERWENT; IBM_TDB			
S60	6	S59 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:58

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S61	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S62	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S63	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S64	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S65	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S66	698	C07C31/20.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S67	251	c07c29/48.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S68	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S69	3196	c07c11/02,107.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S70	2105	B01J21/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S71	2140	c07c2521/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S72	2	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S69	USPAT	OR	OFF	2020/04/03 13:07
S73	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S66	USPAT	OR	OFF	2020/04/03 13:09
S74	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S65	USPAT	OR	OFF	2020/04/03 13:10
S75	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S67	USPAT	OR	OFF	2020/04/03 13:10
S76	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S68	USPAT	OR	OFF	2020/04/03 13:10

4/3/2020 3:36:43 PM
C:\Users\ycutliff\Documents\EAST\Workspaces\16262898.wsp

UNITED STATES PATENT AND TRADEMARK OFFICE

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United States Patent and Trademark Office
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P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

BIB DATA SHEET

CONFIRMATION NO. 3410

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
16/262,898	01/30/2019	568	1622	I0113-198U1

APPLICANTS

Inolex Investment Corporation, Wilmington, DE

INVENTORS

Rocco V. Burgo, Mullica Hill, NJ;
Michael E. Wright, Hurricane, UT;
Gary B. Mosser, Tabernacle, NJ;
Michael J. Fevola, Belle Mead, NJ;

**** CONTINUING DATA ***************************

This appln claims benefit of 62/623,985 01/30/2018

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

02/15/2019

Foreign Priority claimed ❑ Yes ☑ No 35 USC 119(a-d) conditions met ❑ Yes ☑ No Verified and Acknowledged /YATE KAI RENE CUTLIFF/ Examiner's Signature	❑ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		NJ	7	41	3

ADDRESS

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053
UNITED STATES

TITLE

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

FILING FEE RECEIVED		
3980	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	❑ All Fees ❑ 1.16 Fees (Filing) ❑ 1.17 Fees (Processing Ext. of time) ❑ 1.18 Fees (Issue) ❑ Other _____ ❑ Credit

ELECTRONICALLY FILED

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Patent Application of: Inolex Investment Corporation			
Conf. No.:	3410	Group Art Unit:	1622
Appln. No.:	16/262,898	Examiner:	Yate Kai Rene Cutliff
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Process for Making the Same		

INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. §1.97(b)

Enclosed is an Information Disclosure Citation Form PTO/SB/08A, which cites documents which may be material to the patentability of this application and/or for which there may be a duty to disclose in accordance with 37 C.F.R. §1.56.

This Information Disclosure Statement is pursuant to 37 C.F.R. § 1.97(b) and being filed within three months of a request for continued examination.

No fee is required, however, should application of a fee be necessary, the Commissioner is hereby authorized to charge the fee and any deficiency to Deposit Account No. 60-2682 (Billing No. I0113.0249).

The filing of this Information Disclosure Statement shall not be construed as an admission that any of the listed documents constitutes prior art, or as an admission against interest in any manner.

It is respectfully requested that this Information Disclosure Statement and the documents listed on the attached Form PTO/SB/08A be considered and acknowledged by the Examiner in connection with the above-identified patent application, be made of record therein, and that the listed documents be cited in the issued patent.

Respectfully submitted,

INOLEX INVESTMENT CORPORATION

05/01/2020 By: /Lynda L. Calderone/
(Date)

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LLC:smc
Enclosures: Form PTO/SB/08A (1 page)

ELECTRONICALLY FILED

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Patent Application of: Inolex Investment Corporation			
Conf. No.:	3410	Group Art Unit:	1622
Appln. No.:	16/262,898	Examiner:	Yate Kai Rene Cutliff
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Process for Making the Same		

FIRST REQUEST FOR CONTINUED EXAMINATION (RCE) UNDER 37 C.F.R. §1.114

This is a first request under 37 C.F.R. §1.114 for continued examination (RCE) of the above-identified application in response to the Notice of Allowance mailed April 13, 2020 and is being timely submitted by May 1, 2020. Enclosed are the following in support of the RCE under 37 C.F.R. 1.114:

[ ] Enter the un-entered Amendment previously filed on ____ under 37 C.F.R. §1.116 in the above application.

[ ] An Amendment and Request for Reconsideration

[X] RCE fee of $1300 required under 37 C.F.R. 1.17(e)(1).

[X] An Information Disclosure Statement, Form PTO/SB/08A and ___ cited references.

[ ] New formal drawings.

[ ] A Petition for Extension of Time for @& month(s) for the pending application.

[ ] Other:

[ ] Applicant(s) are incurring additional claim fees of ____ for excess claims submitted in the enclosed Amendment, which are calculated as follows:

					MICRO ENTITY		SMALL ENTITY		LARGE ENTITY	
	CLAIMS REMAINING AFTER AMENDMENT		**HIGHEST NO. PREVIOUSLY PAID FOR**	**EXTRA**	**RATE**	**ADDIT. FEE**	**RATE**	**ADDIT. FEE**	**RATE**	**ADDIT. FEE**
TOTAL		-			X $25		X $50	$	X $100	
INDEP.		-			X $115		X$230	$	X $460	

[ ] 1st PRESENTATION OF MULTIPLE DEPENDENT CLAIMS	$205		$410		$820	
			TOTAL	**$**	**TOTAL**	

[X] The applicant(s) herewith pay the following fees totaling $1,300 by charging credit account Calderone Bullock credit card (Billing No. I0113.0249):

[X] First RCE fee in the amount of $1300.

[ ] Extension fee in the amount of $0.

[ ] Additional claim fee(s) in the amount of $0 as calculated above.

[X] The Commissioner is hereby authorized to charge and/or credit Deposit Account No. 60-2689 (Billing No. I0113.0249) as noted below.

[X] Any overpayments or deficiencies in the calculated fee(s).

[X] Any additional fees required under 37 C.F.R. §§ 1.16 or 1.17.

[X] In the event that a Petition for Extension of Time is required, but not enclosed, please charge any extension fee under 37 C.F.R. § 1.136(a) to our Deposit Account noted above.

Respectfully submitted,

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Enclosures: Information Disclosure Statement, SB08A and references

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In Re Patent Application of: Inolex Investment Corporation			
Conf. No.:	3410	Group Art Unit:	1622
Appln. No.:	16/262,898	Examiner:	Yate Kai Rene Cutliff
Filing Date:	January 30, 2019	Attorney Docket No.:	I0113-198U1
Title:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Process for Making the Same		

INFORMATION DISCLOSURE STATEMENT UNDER 37 C.F.R. §1.97(b)

Enclosed is an Information Disclosure Citation Form PTO/SB/08A, which cites documents which may be material to the patentability of this application and/or for which there may be a duty to disclose in accordance with 37 C.F.R. §1.56.

This Information Disclosure Statement is pursuant to 37 C.F.R. § 1.97(b) and being filed within three months of a request for continued examination.

No fee is required, however, should application of a fee be necessary, the Commissioner is hereby authorized to charge the fee and any deficiency to Deposit Account No. 60-2682 (Billing No. I0113.0249).

The filing of this Information Disclosure Statement shall not be construed as an admission that any of the listed documents constitutes prior art, or as an admission against interest in any manner.

It is respectfully requested that this Information Disclosure Statement and the documents listed on the attached Form PTO/SB/08A be considered and acknowledged by the Examiner in connection with the above-identified patent application, be made of record therein, and that the listed documents be cited in the issued patent.

Respectfully submitted,

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Form PTO/SB/08A				Complete if Known	
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U.S. PATENT DOCUMENTS				
Exr Initials	U.S. Patent Document Number	Kind Code (if known)	Name of First Inventor of Cited Document	Date of Publication of Cited Document MM-YYYY
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Exr Initials	Foreign Patent Document Country Code	Number	Kind Code (if known)	Name of Applicant of Cited Document	Date of Publication of Cited Document MM-YYYY	T_1
	WO	2004/078336	A2	Ziehe	09-2004	
	WO	2013/077904	A1	Wright	05-2013	
	WO	2013/106065	A1	Wright	07-2013	
	CN	105312044	B1	Jin	02-2018	

OTHER PRIOR ART - NON PATENT LITERATURE DOCUMENTS		
Exr Initials	Include Name of first Author (in CAPITAL LETTERS), title of the article (where appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), volume-issue number(s), page(s), date (in parentheses). If a book, also include publisher and city and/or county where published.	T_1
	DAI LU, Directing enzyme devolution for biosynthesis of alkanols and 1,n-alkanediols from natural polyhydroxy compounds, Metabolic Engineering. 1 Nov 2017, Vol. 44, p. 77, Fig 7a	
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	ASTMD6866-05, Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotape Ratio Mass Spectrometry Analysis, March 1, 2005	

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(54) Title: PROCESS FOR THE DEHYDRATION OF ALCOHOLS YIELDING α-OLEFINS

(57) Abstract: The present invention relates to a process for producing a-olefins by dehydration of alcohols in the presence of γ-alumina. Furthermore, this invention relates to the use of γ-alumina as a dehydration catalyst.

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PROCESS FOR THE DEHYDRATION OF ALCOHOLS YIELDING α -OLEFINS

The present invention relates to a process for producing α-olefins by dehydration of alcohols in the presence of γ–alumina. Furthermore, this invention relates to the use of γ–alumina as a dehydration catalyst.

Linear α-olefins are produced on a large scale for example by ethylene oligomerisation, Fischer-Tropsch synthesis or, as in the case of 1-hexene, by controlled trimerisation. The ethylene oligomerisation can be performed for example according to Ziegler by a two-stage process, i.e. by a building-up reaction using triethyl aluminium, followed by 'short-time high-temperature displacement' (termed ALFEN process), or by a single-stage high-temperature process with triethyl aluminium catalysis.

Another process for producing α-olefins is the dehydration of alcohols, which has been described in detail for example by Knözinger, H., *Angew. Chem. (Applied Chemistry), Int. Ed.*, vol. 7, 1968, no. 10, p. 791-805.

Short-chain linear α-olefins are especially employed as co-monomers for making polyethylene copolymers. High purity is essential for this use, particularly as regards the 1-olefins content, plus the lowest possible amount of impurities, such as internal, branched, or cyclic alkenes, and dienes or alkines. It is known that few ppm of impurities already result in rapid deactivation of the polymerisation catalyst. Owing to the small boiling-point difference of the double-bond isomers and structural isomers of the olefins, which makes splitting by distillation expensive, the α-selectivity of the dehydration step is most important.

By the term 'α-selectivity' as used herein is meant the ratio of the α-olefin formed to the total olefins formed, i.e. the total of α-olefins, internal, branched, and cyclic olefins.

Suitable alumina catalysts for this application comprise for example zinc- and zirconium-doped aluminas (cf. e.g. U.S. patent 4,260,845; EP patent 0 150 832-B1, respectively). The α-selectivity can also be improved by addition of bases, which, however, has an adverse effect on the reactivity. For example, base-doped alumina

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catalysts, such as barium-doped alumina, require significantly higher temperatures than the corresponding undoped catalysts. Acidic aluminas can be used at considerably lower temperatures causing, however, more isomerisation reactions and hence a decrease in α-selectivity.

Furthermore, it is known that there are processes, wherein prior to use the bases are homogeneously mixed with the alcohol. German patent DE 39 15 493 C2 describes the improvement of α-selectivity in the dehydration of fatty alcohols on γ-alumina by addition of 20 to 300 ppm of ammonia. However, it is a disadvantage of said process to add an additional component, namely ammonia, which later must be separated.

The commonly known processes of alumina-catalysed dehydration have the disadvantage of poor α-selectivity obtained with the customary catalysts. The selectivity can be improved at the expense of the turnover or by costly modification of the catalyst or by additon of further substances, which later must be separated. Moreover, reaction temperatures of greater than 350°C are necessary in order to achieve a fairly good conversion.

It is, therefore, an object of the present invention to provide a process for producing α-olefins by dehydration of alcohols, which process yields a high α-selectivity and good conversion at a low reaction temperature of less than 350 °C, particularly 320 °C and lower, without addition of bases or acids or without catalyst doping. Another object of the present invention is to provide a novel dehydration catalyst.

According to the present invention, the problem has been solved by a process for producing α-olefins by dehydration of alcohols in the presence of γ-alumina, wherein the alcohol is brought into contact with at least one γ-alumina having

- a pore volume of greater than 0.9 ml/g, preferably greater than 1.0 ml/g (measured in accordance with DIN 66133, contact angle 131°C),
- at least one pore radii maximum in the mesopores range (10 to 250 Å) from 20 to 90 Å, preferably 30 to 80 Å, and
- at least one additional pore radii maximum in the macropores range (greater than 250 Å).

The dehydration is preferably carried out at temperatures in the range from 260 to 350 °C, most preferably from 280 to 320 °C. The preferred embodiments of the subject invention are set out in the subordinate claims or hereinbelow.

According to the invention, the preferable alcohols are comprised of linear or branched 1-alkanols having 4 to 14 carbon atoms. Examples of suitable 1-alkanols include 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, 2-ethyl-1-hexanol, and 2-butyl octanol, of which 1-hexanol and 1-octanol are particularly preferred.

In addition to all-γ-phase alumina, catalyst blends composed of γ- and δ-phases may be used as well. The γ-alumina according to the invention is mostly comprised of the γ-phase, namely, more than 50 wt%, preferably more than 90 wt%, and it has a bimodal pore radii distribution comprising at least one pore radius maximum in the mesopores range (pore radius 10 to 250 Å) and one in the macropores range (pore radius > 250 Å) with a total pore volume of greater than 0.9 ml/g and an amount of mesopores of preferably greater than 0.6 ml/g (determined in accordance with DIN 66133 by the mercury intrusion method at a contact angle of 131°). At least one maximum of the mesopores radii distribution of the γ-alumina of the invention is in the range from 20 to 90 Å, preferably 30 to 80 Å, whereas the preferable maximum of the macropores is greater than 1,000 Å.

It is preferable to use alumina having an Al_2O_3 content of >99 wt%, which unlike the aluminas described in US 4,260,845 or EP 0 150 832-B1, is not doped with zinc or zirconium or other additives, a process-conditioned amount of zinc and zirconium of typically less than 10 ppm notwithstanding. It is furthermore preferable not to employ any other type of dehydration catalysts, including co-catalysts or active carriers.

An example of a typical composition of the catalysts of the invention is given in Table I hereinbelow.

Table I

Catalyst Composition	PURAL™ KR 1	
Al	wt%	53.6
Si	ppm	553
Ca	ppm	176
Na	ppm	159
Fe	ppm	156
Mg	ppm	78
Ga	ppm	70
Ti	ppm	14
Pb	ppm	14
Cr	ppm	11
K	ppm	<10
Li, Zr, B, Mo, Ni, Mn, Zn,Cu,Co	each ≤ 5 ppm	

In principle, any commercially available γ-alumina catalyst can be employed for the dehydration of 1-alcohols, but their use is less advantageous, compared to the catalysts of the invention. The γ-Al_2O_3-catalysts of the invention differ from conventional catalysts in their physical properties, such as surface, porosity, pore geometry, and chemical composition. The catalysts of the invention excel by their high pore volume of greater than 0.9 ml/g and pore radii distribution which is at least bimodal and has at least one maximum in the mesopores range from 30 to 80 Å and one in the macropores range of preferably >1,000 Å, wherein the pore volume of the mesopores preferably makes up more than 40 % of the total pore volume, whereas independently thereof the pore volume of the macropores preferably constitutes more than 20 %. In the dehydration of 1-alcohol the special combination of physical properties of this alumina surprisingly yields a crude product having a significantly higher α-selectivity with unimpaired conversion (cf. Table II).

The γ-alumina catalysts of the invention are different from the conventional catalysts usually employed for the dehydration of 1-alcohols yielding 1-olefins, because they have been modified by the manufacturing method, especially with respect to their physical properties, such that they have turned out to be

surprisingly selective in the dehydration process, particularly as regards the purity of the desired 1-olefin.

The process of the invention is preferably carried out at a pressure ranging from 10 to 2,000 mbar. The high-porosity alumina is preferably employed for example in the form of beads, extrudate clippings, granules, or pellets. The dehydration is preferably carried out continuously, most preferably in a continuous tube reactor.

The process of the invention can be carried out for example as follows:

The preferably gaseous alcohol is passed preferably at 280 to 320 °C through a reactor, especially a tube reaetor, packed with the alumina of the invention. Pressure and temperature are such that at the reaction conditions of choice the catalyst is not contacted by liquid, e.g. the higher-boiling ether, which may theoretically be formed as an intermediate during the reaction. The alcohol may optionally be mixed with inert gas, e.g. nitrogen. The alumina is present for the most part as a g-phase material, preferably in the form of granules, extrudate, or beads.

The reaction product is condensed, the aqueous phase is separated, and the organic phase is analysed by gas chromatography in order to examine the reaction. With the purpose of evaluating the catalyst activity, the reactor is operated at steady conditions until a constant composition/stationary state is reached. The organic phase obtained after phase separation is distilled and both the unreacted alcohol and the dialkyl ether formed can be recycled to the process. Alternatively, the alcohol/dialkyl ether mixture can be separated from the olefin/water mixture by condensation immediately after the reaction, followed by direct recycling to the process.

The dihexyl ether which is usually formed as a by-product during the reaction of 1-hexanol can be distilled off and recycled to the process. The compositions of the crude educts/products and the test conditions for various catalysts have been compiled in Table II .

PURAL™ KR1 granules and extrudates are exemplary of the high-prosity bimodal γ-aluminas of the invention. When comparing the α-selectivities at 300 °C and a feed rate of 2 ml/min, their remarkable superiority over the

Südchemie catalyst is obvious. This superiority is yet more evident at 325 °C. PURAL™ KR2, too, is a high-porosity γ-alumina, but with a monomodal pore radii distribution. The P 180 catalyst is a high-porosity alumina, but compared with the catalyst of the invention, it has a considerably greater average pore radius in the mesopores range.

It has become apparent that the process for producing 1-hexene in the co-monomer mode utilising the alumina according to the invention is much more cost-effective. For example, working-up of the crude product by distillation in order to obtain a 1-hexene content of > 99 % can be accomplished by means of a column with fewer separation stages. The turnover can be affected by temperature, feed quantity (MHSV), and catalyst bed length, but the α-selectivity decreases as the turnover increases.

Figure 1 shows the pore radii distributions of PURAL™ KR1 according to example 3 and of PURAL™ KR2 according to comparative example 4. The pore radii were determined by the Hg intrusion method according to DIN 66133 at a contact angle of 131° using a measuring apparatus of *micromeritics* company.

Figure 2 shows the 1-hexene content in the crude product versus the α-selectivity as a function of feed quantity and temperature. The data points plotted for a 1-hexene content of less than 30 % have been obtained at 300 °C, whereas the data collected for a 1-hexene content of greater than 30 % are based on 325 °C (legend: (1) 300°C, 2 ml/min; (2) 325°C, 3 ml/min; (3) 325°C, 2 ml/min; (4) 325°C, 1 ml/min). With an increasing turnover the differences in the α-selectivities of various catalysts become particularly plain.

Examples

Preparation of γ-Al_2O_3 Extrudates

2 kgs of alumina and 2 kgs of water were mixed for 20 minutes in a Z-type kneader mixer. The resultant paste was extruded through a 2-mm strainer of a single-screw extruder and then was dried and calcined onto the desired surface.

Preparation of γ-Al_2O_3 Granules

Alumina and water were continuously mixed in a double-screw extruder at a feed rate of 15 kgs/h. The resultant granules were dried and then calcined onto the desired surface.

Examples 1 through 5 **Dehydration of Hexanol on Alumina**
(for the specification, see Table II)

In a continuously operated tube reactor (23 mm in diameter, 100 mm in length), 2 ml/min of hexanol vapour having a purity of 99.4 % and 0.25 l/min of nitrogen were passed at 300 °C/325 °C and 2 bar through a 50-mm catalyst bed comprised of 7.2 to 9.9 grams of catalyst, depending on the bulk density.

When using the monomodal γ-alumina of Südchemie (CS 331-1; pore volume 0.82 ml/g) at 300°C reaction temperature, the organic phase obtained after phase separation of the crude product comprised 44.2 % hexanol, 32.2 % dihexyl ether, and 20.7 % 1-hexene (comparative example 4). The α-selectivity was 96.5 %.

When using PURAL™ KR1 at 300°C reaction temperature, the organic phase obtained after phase separation of the crude product comprised 35.2 % hexanol, 38.7 % dihexyl ether, and 24.5 % 1-hexene. The α-selectivity of the hexenes was 97.7 %.

Table II

Gas-Phase Dehydration of 1-Hexanol on Al_2O_3 Catalysts

Examples	1		2		3	4	5
Catalyst Al_2O_3	CS 331-1 (Südchemie)		PURAL KR1 (Sasol)		PURAL KR1 (Sasol)	PURAL KR2 (Sasol)	P180 (Sasol)
Type	Extrudates		Granules		Extrudates	Extrudates	Extrudates
Surface (m^2/g)	235		184		232	215	157
Pore volume (Hg) [ml/g], thereof pore radii of	0.83		1.31		1.28	0.89	0.99
< 300 Å	0.69 (83%)		0.79 (60%)		0.77 (60%)	0.84 (94%)	0.77 (78%)
300 – 1,000 Å	0.04 (5%)		0.05 (4%)		0.03 (2%)	0.01 (2%)	0.03 (3%)
> 1,000 Å	0.09 (11%)		0.47 (36%)		0.48 (38%)	0.04 (4%)	0.19 (19%)
Pore radius maximum > 1,000 Å	1,000		2,500		5,000	-	≈ 5,000 (large distribution)
Pore radius maximum < 1,000 Å	50		68/49		50/35	70/40	117
Temperature [°C]	**300**	**325**	**300**	**325**	**325**	**325**	**325**
Feed quantity [ml/min]	2	2	2	2	2	2	2
Composition [wt%]							
1-Hexanol (educt 99.40)	44.22	24.77	35.21	19.03	21.14	21.83	24.25
Dihexyl ether	32.23	14.78	38.65	18.75	15.40	14.33	13.76
1-Hexene	20.704	52.551	24.517	58.421	58.840	58.653	55.90
cis-2-Hexene	0.518	4.210	0.412	1.839	2.320	2.668	3.49
trans-2-Hexene	0.180	1.483	0.116	0.530	0.826	1.007	1.32
cis-3-Hexene	0.013	0.118	0.010	0.046	0.066	0.085	0.08
trans-3-Hexene	0.011	0.103	0.008	0.037	0.056	0.076	0.19
2-Ethyl-1-butene	0.013	0.015	0.016	0.025	0.024	0.022	n. a.
3-+4-Methyl-1-pentene	0.003	0.009	0.003	0.008	0.009	0.009	n. a.
3-Methyl-2-pentene	0.003	0.012	0.002	0.009	0.008	0.010	n. a.
Total of other hexenes	-	-	-	-	-	-	0.31
Total of C_6 olefins	21.45	58.50	25.08	60.92	62.15	62.53	61.29
Conversion [%]	55.52	75.08	64.58	80.86	78.74	78.04	75.60
α-Selectivity [%]	96.54	89.83	97.74	95.91	94.68	93.80	91.21

5

Patent Claims

1. A process for producing α-olefins by dehydration of alcohols in the presence of γ-alumina,
characterised in that the alcohol is brought into contact with at least one γ-alumina having
   - a pore volume of greater than 0.9 ml/g,
   - at least one pore radii maximum in the mesopores range from 20 to 90 Å, and
   - at least one pore radii maximum in the macropores range, i.e. greater than 250 Å.

2. The process according to claim 1,
characterised in that the pore volume of the mesopores in ml/g (pore radii from 10 to 250 Å) of the γ-alumina makes up more than 40 % of the total γ-alumina pore volume.

3. A process according to any one of the preceding claims,
characterised in that the pore volume of the macropores in ml/g (pore radii greater than 250 Å) of the γ-alumina makes up more than 20 % of the total γ-alumina pore volume.

4. A process according to any one of the preceding claims,
characterised in that the pore volume of the mesopores (pore radii from 10 to 250 Å) of the γ-alumina is greater than 0.6 ml/g.

5. A process according to any one of the preceding claims,
characterised in that the pore volume of the macropores (pore radii greater than 250 Å) of the γ-alumina is greater than 0.3 ml/g.

6. A process according to any one of the preceding claims,
characterised in that the γ-alumina comprises more than 99 wt% Al_2O_3.

7. A process according to any one of the preceding claims,
characterised in that the dehydration is performed at temperatures ranging from 260 to 350 °C, preferably 280 to 320 °C.

8. The process according to any one of the preceding claims, characterised in that the alcohol employed herein is a linear alcohol, preferably at least one linear alcohol selected from the group consisting of 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol and 1-tetradecanol.

9. A process according to any one of the preceding claims, characterised in that the alcohol employed herein is comprised of one or more 1-alkanol(s) having 4 to 14 carbon atoms, particularly 6 to 8.

10. A process according to any one of the preceding claims, characterised in that the γ-alumina is employed in the form of blanks, preferably as beads, pellets, extrudate, or granules, and independently thereof preferably in a fixed-bed reactor.

11. A process according to any one of the preceding claims, characterised in that the alcohol is in the gas phase when contacted with the γ-alumina.

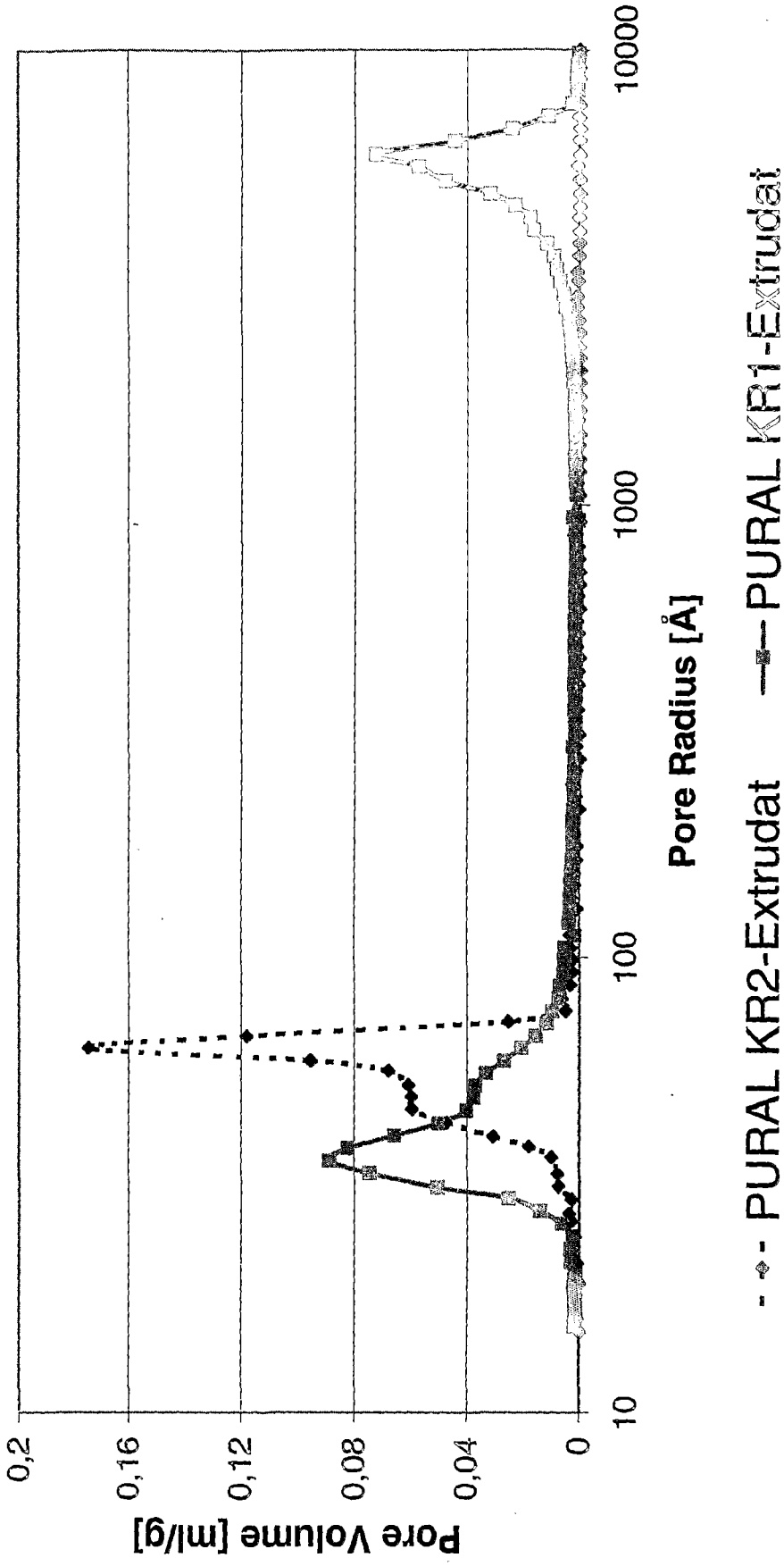
12. A process according to any one of the preceding claims, characterised in that the dehydration is performed at a pressure of 10 to 2,000 mbar.

13. A process according to any one of the preceding claims, characterised in that the dehydration is continuously performed in a tube reactor.

14. A process according to any one of the preceding claims, characterised in that at least one pore radii maximum is found in the macropores range with pore radii of greater than 1,000 Å.

15. The use of any one of the γ-aluminas claimed in any one of the preceding claims as a dehydration catalyst.

Fig. 1


Incremental Pore Volume
Pore Volume [ml/g]
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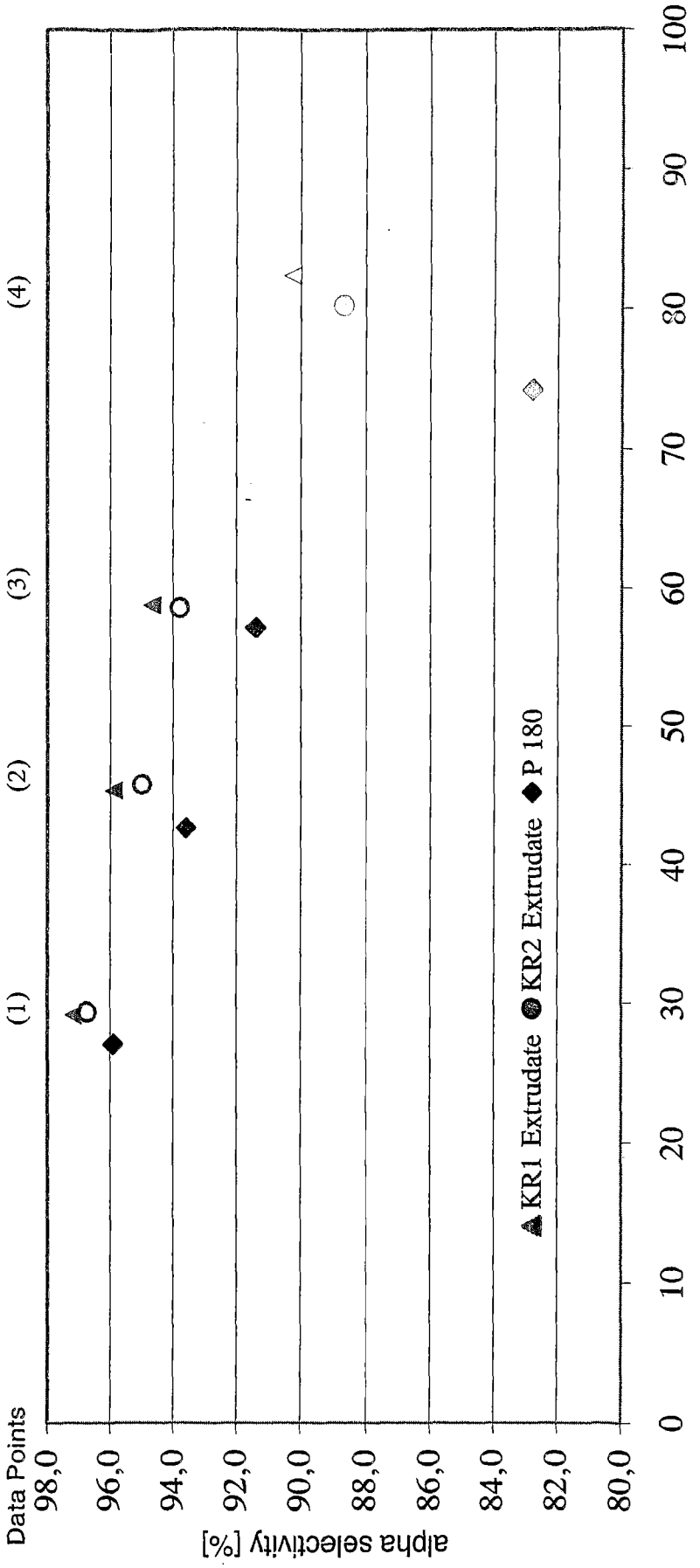
Pore Radius [Å]
- PURAL KR2-Extrudat
PURAL KR1-Extrudat

Fig. 2


Data Points
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alpha selectivity [%]
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20
30
40
50
60
70
80
90
100
1-Hexene Content [%]
KR1 Extrudate
KR2 Extrudate
P 180

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(54) **Title**: WATER AND CONTAMINANTS REMOVAL FROM BUTANOL FERMENTATION SOLUTIONS AND/OR BROTHS USING A BRINE SOLUTION

(57) **Abstract**: A process and apparatus are provided for removal of water and other selected contaminants from butanol fermentation broths which can be achieved by continuous extraction with a concentrated salt solution with a regulated pH value. This process greatly reduces distillation energy and losses for the final purification of butanol (normal or iso-). Furthermore, this process allows for generation of sufficiently pure biobutanol (>97%) for use in a subsequent chemical process.

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WATER AND CONTAMINANTS REMOVAL FROM BUTANOL FERMENTATION SOLUTIONS AND/OR BROTHS USING A BRINE SOLUTION

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

[0002] The invention generally relates to a fuel and process for dewatering and purifying butanol prepared through a fermentation process.

BACKGROUND

[0003] Purification of butanol from fermentation processes has a long history, nearly as long at the initial discovery of the Acetone-Butanol-Ethanol process by Louis Pasteur in 1862. What has evolved as the most efficient purification process involves some kind of sparge using an inert carry stream. This can be carbon dioxide or simply water. One practiced method takes advantage of the butanol-water azeotrope. This azeotrope, after collection, then phase separates into an organic phase (top) and a bottom water layer. The organic phase is often denoted as the "butanol beer broth," which is decanted away from the bottom water layer. The latter is returned and can be used again as a sparging solvent.

[0004] US Patent Application 12/018,216 summarizes the four general methods of purifying butanol as related to iso-butanol, although the methodology is applicable to both iso- and n-butanol.

[0005] The first method takes the organic layer including butanol and ~15-20 water is simply further purified by fractional distillation. The first fractions are low boiling impurities followed by azeotropic (butanol-water) removal of the water and this is followed by collection of the purified butanol, typically 98% or greater. The butanol-water azeotrope is recycled and must be

distilled again, utilizing process time and energy.

[0006] In method two, the butanol is isolated from the fermentation medium using liquid-liquid extraction in combination with distillation. In this method, the butanol is extracted from the fermentation broth using liquid-liquid extraction with a suitable solvent. The butanol-containing organic phase is then distilled to separate the butanol from the solvent. This method can require large amounts of a flammable co-solvent and presents difficulties with scale.

[0007] In method three, a distillation in combination with adsorption is used to sequester butanol from the fermentation medium. For this process, the fermentation broth containing the butanol is sparged near the azeotropic composition and then the remaining water is removed by use of an adsorbent, such as molecular sieves (Aden et al., Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover, Report NREL/TP-510-32438, National Renewable Energy Laboratory, June **2002**). This can require large amounts of absorbent since butanols typically carry 15-20 wt. % water once physically separated from the water phase.

[0008] A fourth approach is to combine a sparging process to first remove the butanol from the reactor and solids followed by a pervaporation process. As above, the fermentation broth containing the butanol (typically 1.0-2 wt. %) is sparged from the bioreactor at approximately azeotropic composition, after phase separation and the remaining water is removed by pervaporation, for example, through a hydrophilic membrane [Guo et al., *J. Membr. Sci.* 245, 199-210 (**2004**)]. Typically pervaporation processes are difficult for large scale operations and can be extremely costly on a commercial scale. When used before a sparging process and contact is made with the fermentation mixture, biofouling of the membrane is problematic.

BRIEF DESCRIPTION OF THE DRAWINGS

[0001] **FIG 1.** A general overview of process going from sugars (fermentation) to purified biobutanol, according to embodiments of the inventions.

[0002] **FIG 2.** A process flow diagram (PFD) for dewatering and contaminant removal from "biobutanol beer broth" obtained as a sparge from a fermentation vessel, according to embodiments of the inventions.

[0003] **FIG 3**. Proton nuclear magnetic resonance (NMR) spectrum of dewatered bio-1-butanol obtained from an original "butanol beer broth" including 15-18 wt. % water. The original broth was obtained by fermentation of sugars using Clostridium bacteria, according to embodiments of the inventions.

[0004] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

DETAILED DESCRIPTION OF EMBODIMENTS OFTHE INVENTION

[0005] The invention generally relates to a process and fuel derived from biobutanol. Biobutanol is butanol that is derived from the fermentation of biomass. It can be as a direct precursor to 1-butene. 1-butene can be utilized to make drop-in JP-5 alternative fuels. Thus, improvements in isolating biobutanol are expected to decrease cost of the alternative JP-5 jet fuel.

[0006] Currently energy intense distillation methods are used to remove water from the biobutanol (as produced in fermentations). A rapid and quick drying with a brine solution can reduce the waste and cost of the associated lengthy distillation process and lead to increased yield of biobutanol.

[0007] Currently distillation alone is used to purify biobutanol on large scale production processes. This is done to remove ethanol, acetone, the predominance of water (~15%), and other minor impurities. By using azeotropic distillation of the butanol followed by, physical separation, and then drying by exposure to a brine solution (saturated sodium chloride or other salts), an almost continuous distillation process can be used and eliminate the primary impurities of the biobutanol.

[0008] An aspect of the invention relates to a purification process of isolating biobutanol including removing biobutanol from a fermentation broth using at least one separation process and phase separating an organic layer and a concentrated biobutanol, dewatering the

concentrated biobutanol, and removing acid components with an aqueous saturated or near-saturated aqueous salt solution, chemically drying the biobutanol with at least one absorbent, and distilling the biobutanol to produce a purified biobutanol product.

[0009] Another aspect of the invention relates to a system that isolates biobutanol including a fermentation vessel that removes biobutanol from a fermentation using a separation system that yields an organic layer of concentrated biobutanol, a dehydrating device that dewaters the concentrated biobutanol and removes acid components with an aqueous saturated or near-saturated aqueous salt solution, a chemical drying device that dries the biobutanol with at least one absorbent, and a distilling system that separates undesired components from the biobutanol to produce a purified biobutanol product.

[0010] Embodiments of the invention further include utilizing at least one inert gas during the separation process. In embodiments, the separation process is selected from the group consisting of a sparging process, membrane separation, and continuous feed by mechanical stirring of said broth. In embodiments, the dewatering includes passing said concentrated biobutanol over a stripper to remove acetone. In embodiments, the salt solution is a brine solution. In embodiments, the distilling system includes a fractionation process. In other embodiments, the distilling process includes a fractionation process having between 1 to 20 theoretical plates, or 10. In embodiments, the aqueous salt solution includes inorganic salts with sodium or potassium ions and negative ions of chloride, sulfate, carbonate, and/or bicarbonate at saturation. The salt solution can have a pH of about 8-10.

[0011] The purified biobutanol product can be about 97-99+% pure 1-butanol. In embodiments, the biobutanol is iso-butanol, using collection method temperatures of about 107-112°C, or 107-110°C. In embodiments, the salt solution is within 80-99% of saturation. In other embodiments, the salt solution is within 80 to 99% of saturation or near saturation, or 95% of saturation. In embodiments, the device that dewaters the biobutanol results in about 1-4% water remaining in the purified biobutanol product. In other embodiments, the dewatering of the biobutanol resulting in about 1-4% water remaining, or 2-3%, in the purified biobutanol product. In another aspect of the invention, a purified biobutanol product is obtained from the process defined above.

[0012] Embodiments of the invention further include utilizing at least one inert gas during the separation system. In embodiments, the separation system is selected from the group consisting of a sparging process, membrane separation, and continuous feed by mechanical stirring of the broth. In embodiments, the dehydrating device includes a stripper to remove acetone.

[0013] Embodiments of the invention can lead to an increase in production yield, simplify the equipment, lower energy use in the purification process, and concurrently eliminating acidic components. The brine solution-drying/purification method can be coupled with other techniques including sparging by carbon dioxide to remove and collect the biobutanol. The latter also requires a complicated distillation that could be mitigated by treatment with the brine solution.

[0014] Typical alternatives could be membrane technology, although this process can suffer from difficulty in running at large scale and continuous operation. As it stands several distillations are required and involve reduced yields from losses in the distillation-only processing. Embodiments of the invention could be employed with other alcohols like pentanol, which is also a target of the fermentation business of making new biofuels.

[0015] An embodiment of the invention includes a method demonstrating a quick and efficient way to remove water and acids from butanol by contacting the organic phase with a near-saturated aqueous salt solution which rapidly dewaters the butanol and removes acid components. This can be followed by chemical drying using a minimum of absorbent and then the product distilled to afford pure butanol with exceptional mass yields and low energy consumption.

[0016] The butanol broth used herein can be prepared by one of several methods known to those skilled in the art of fermentation. Typically, once a maximum titer is achieved in the fermentation vessel, the butanol is removed in some form of a sparging process whereby the butanol is concentrated and then phase separates as an organic layer that can include by-products of the fermentation process that may have organic chemicals/contaminants including, but not limited to, acetone, ethanol, furans, acetic acid, butyric acid, and various esters. Depending on the mixture's exact composition, 15-20 wt. % of water will also remain in the butanol. While 15-20 wt. % is a common amount of the remaining water, water contents from

5 to 40 wt. % are generally acceptable.

[0017] The near-saturated or saturated salt solution used herein can be formed by treating water with an excess amount of an inorganic salt. Typical inorganic salts that can be used include sodium and potassium ions with negative ions of one or more of chloride, sulfate, carbonate, and bicarbonate, and combinations thereof, but the method is not limited to these. One factor for the resulting salt solution is that it be sufficiently close to or at saturation. Once in process, the aqueous salt solutions can be brought to near saturation by evaporation water by an active heating/evaporation process, outdoor evaporation in open ponds, or in a recycling system using evaporation to remove water and concentrate the salt solution. Near saturation generally refers to a salt solution in which at least one inorganic salt is present at concentration sufficient for the salt solution, at the temperature when it is in contact with the broth, to be at 90% or more of the theoretical weight present at full saturation, such as at least 95% or at least 98 wt. % of the theoretical weight.

[0018] The salt solution is brought to a pH of 8-10, such as about 8. The basic salt solution is brought in contact with the butanol sparge feed and mixed thoroughly by mechanical stirring for a period of 5 to 30 min, e.g., 15 min. The top organic phase is the dewatered butanol, with any acid contaminants being removed into the salt solution. The top organic phase is passed over a stripper to remove acetone and then transferred through an optional secondary drying column and then on to a continuous distillation column for final fractionation. The bio-n-butanol can be further dried with exposure to a drying agent. This can bring the water content to below1% (by weight). Collection of butanol from a 113-117 °C fraction affords 97-99+ % pure 1-butanol with capture of 90-99% of the theoretical biobutanol included in the "biobutanol beer broth." Similar results can be obtained for iso-butanol using an identical process except collecting a fraction at 107-110 °C. The bottoms in the final and only distillation can be discarded in the process and typically represent 1-2 wt. % of the volume of purified butanol. They typically include salt residue that can be recycled.

[0019] In **FIG 1**, a general overview of process/apparatus going from sugars (fermentation) to purified biobutanol is shown. Biomass**10** undergoes a fermentation process and at S100 initial removal of biobutanol takes place to provide crude biobutanol **12**. At S102, azeotropic or other

distillation may take place. Other organic components may be phase separated from the biobutanol. The low cut **14** is taken which is an azeotropic mixture of biobutanol and water and may include other products of the fermentation. At S104, this fraction **14** is treated with a brine solution at or near saturation. Additional salt may be added to the contacting brine solution to ensure the brine is as close to saturation as possible. The salt/water **18** and biobutanol layer **18** are allowed to separate and at S106, the top biobutanol layer 18 is taken and may be subjected to further separation methods at S106, such as drying in a drying column and a final distillation to yield biobutanol **22**. The brine solution **16** may be treated at S108to recover the salt for reuse.

[0020] **FIG 2** shows a process flow diagram (PFD) and apparatus for dewatering and contaminant removal from "biobutanol beer broth" obtained as a sparge from a fermentation vessel **30**. The sparge feed is distilled in an azeotropic distillation apparatus **30** and the azeotropic biobutanol feed is treated with salt in a tank **32** and the salt solution is fed to a concentrator (e.g., evaporator) **34** where excess water is removed by evaporation and/or additional salt is added to maintain the salt solution at or near saturation. The concentrator **34** is configured for regulating the pH of the aqueous salt solution to maintain a predetermined pH (8-10) or salt concentration (within a predetermined range of saturation (e.g., 95 wt. % -100%) in the aqueous salt solution within the dewatering device **34**.

[0021] The saturated solution is then returned to the tank **32**. The salt solution concentration can be a continuous or semi-continuous process. The biobutanol feed is fed to a stripper **36**, where acetone is removed from the feed. The treated biobutanol feed is passed through a drying column **38** and the further dried biobutanol feed is fed to a distillation column **40**, where a butanol-rich fraction is removed which can be at least 97 wt. %, or at least 98 wt. %, or at least 99 wt. % butanol.

[0022] **FIG 3**. Proton nuclear magnetic resonance (NMR) spectrum of dewatered bio-1-butanol obtained from an original "butanol beer broth" including 15-18 wt. % water. The original broth was obtained by fermentation of sugars using Clostridium bacteria.

Example

[0023] At S100, bio-n-butanol is removed from the fermentation vessel **28** by a process of a) sparging with an inert gas, b) membrane separation, and/or c) some other physical means that

will remove the bacteria, yeast, or fungi and remove water and concentrate the biobutanol component.

[0024] At S102, the bio-n-butanol azeotrope (~55% butanol, 45% water, b.p. 97 °C) is carefully distilled using an apparatus **30** with sufficient theoretical separation plates to minimize additional water (bp 100 deg C) co-distilling with the azeotrope. In addition to the bio-n-butanol azeotrope other organics and azeotropes will lead the distillation run. They can be discarded or left in the distillate and will be removed in subsequent steps.

Version A

[0025] At S104, after settling, the azeotrope will form two layers, sodium chloride is added at a sufficient amount to saturate the water layer, the layers are separated and the butanol is isolated by a quick physical separation and can be used in certain processes, for example, dehydration to form bio-1-butene.

Version B

[0026] At S104, the water layer can be separated (discarded or used in a slower secondary process to remove the butanol) from the biobutanol, leaving a water saturated biobutanol. This biobutanol is treated with a saturated salt solution, typically in the range of 10-50% of the volume of the butanol volume, thus removing most of the water. The layers are separated by quick physical separation and the brine solution can be strengthened (i.e. salt added and/or water evaporated off) and used many times.

[0027] At S106, an optional secondary process to remove additional water can be utilized. This can be 3A mol-sieves or a related solid-phase drying agent that can be recycled in service by heating or similar. **Fig. 3** shows a typical dried bio-n-butanol sample using this process.

[0028] Depending on the biobutanol specs, a final distillation to remove last traces of water, ethanol, acetone, and other minor impurities may be desirable. For many applications, this biobutanol may be of sufficient purity, for example use in preparing biobutene that is useful in making diesel and jet fuels and biolubricants.

[0029] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between

any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

CLAIMS

What is Claimed is:

1. A purification process of isolating biobutanol, comprising:

removing biobutanol from a fermentation broth using at least one separation process to phase separate a concentrated organic layer which includes biobutanol;

dewatering said concentrated biobutanol and removing acid components with a saturated or near-saturated aqueous salt solution;

chemically drying said biobutanol with at least one absorbent; and

distilling said biobutanol to produce a purified biobutanol product.

2. The process according to claim 1, further characterized by utilizing at least one inert gas during the separation process.

3. The process according to claim 1, further characterized by said separation process being selected from the group consisting of a sparging process, membrane separation, and continuous feed by mechanical stirring of said broth.

4. The process according to claim **1**, further characterized by said dewatering includes passing said concentrated biobutanol over a stripper **36** to remove acetone.

5. The process according to claim 1, further characterized by said aqueous salt solution including at least one inorganic salt of sodium or potassium ions with negative ions of at least one of chloride, sulfate, carbonate, and bicarbonate.

6. The process according to claim 1, further characterized by said salt solution being a brine solution.

7. The process according to claim 1, further characterized by said salt solution being at

saturation.

8. The process according to claim 1, further characterized by said salt solution including at least one of sodium or potassium cations with negative ions of at least one of chloride, sulfate, carbonate, and biocarbonate and which is maintained within 80 to 99% of saturation, or within 95% of saturation.

9. The process according to claim 1, further characterized by regulating the pH of the salt solution to have a pH of 8-10.

10. The process of claim 1, further characterized by the dewatering including recycling the salt solution through a concentrator device **34** which increases a concentration of salt in the salt solution and returning the more concentrated salt solution for dewatering the concentrated biobutanol.

11. The process according to claim 1, further characterized by said distilling process including a fractionation process having between 1 to 20 theoretical plates, or 10.

12. The process according to claim 1, further characterized by said purified biobutanol product being at least 97% pure 1-butanol, or at least 98% or at least 99% pure 1-butanol.

13. The process according to claim 1, further characterized by said purified biobutanol product being at least 97% pure 2-butanol, or at least 98% or at least 99% pure 2-butanol.

14. The process according to claim 1, further characterized by said biobutanol being iso-butanol and the distilling includes collecting a fraction at a temperature of 107-112°C.

15. The process according to claim 1, further characterized by said biobutanol being 1-butanol and the distilling distilling includes collecting a fraction at a temperature of 113-117 °C.

16. The process according to claim 1, further characterized by said dewatering of said biobutanol resulting in up to 4% water remaining in said purified biobutanol product.

17. The process according to claim 16, further characterized by said dewatering of said biobutanol resulting in 1-4% water remaining, or 2-3% water remaining, in said purified biobutanol product.

18. The process according to claim 1, further characterized by said dewatering being used for continuous extraction from a feed of the concentrated biobutanol.

19. A purified biobutanol product obtained from the process defined in any one of claims 1-18.

20. A system that isolates biobutanol, comprising:

a fermentation vessel **28** that removes biobutanol from a fermentation using a separation system **30** that yields an organic layer **14** of concentrated biobutanol;

a dehydrating device **32** that dewaters a said concentrated biobutanol and removes acid components with a saturated or near-saturated aqueous salt solution;

a chemical drying device **38** that dries said biobutanol with at least one absorbent; and

a distilling system **40** that separates undesired components from said biobutanol to produce a purified biobutanol product.

21. The system according to claim 20, further characterized by utilizing at least one inert gas during the separation system.

22. The system according to claim 20, further characterized by said separation system being selected from the group consisting of a sparging process, membrane separation, and continuous feed by mechanical stirring of said broth.

23. The system according to claim 20, further characterized by said dehydrating device including a stripper to remove acetone.

24. The system according to claim 20, further characterized by said salt solution being a brine solution.

25. The system according to claim 20, further characterized by said distilling system including a fractionation system.

26. The system according to claim 20, further characterized by said salt solution including an inorganic salt solution containing sodium or potassium ions with negative ions of at least one of chloride, sulfate, carbonate, and bicarbonate.

27. The system according to claim 20, further characterized by said salt solution having a pH of 8-10.

28. The system according to claim 20, further characterized by said purified biobutanol product being at least 97% pure 1-butanol.

29. The system according to claim 20, further characterized by said biobutanol being iso-butanol and said distilling system configured for collection of a fraction at a temperature of 107-112°C.

30. The system according to claim 20, further characterized by a concentrator **34** which maintain said salt solution being within 80-99% saturation, by at least one of evaporating water and adding salt to provide sodium or potassium ions with negative ions of at least one of chloride, sulfate, carbonate, and biocarbonate.

31. The system according to claim 20, further characterized by said dehydrating device **32**

dewatering said biobutanol resulting in 1-4% water remaining in said purified biobutanol product.

32. The system according to claim 20, further characterized by the dehydrating device **32** being configured for extraction from a continuous feed of the concentrated biobutanol.

32. The system according to claim 30, further characterized by the concentrator device **34** being configured for regulating the pH of the aqueous salt solution to maintain at least one of a predetermined pH and a predetermined salt concentration in the aqueous salt solution within the dewatering device **32**.

33. The system according to claim 30, further characterized by the predetermined pH being 8-10.

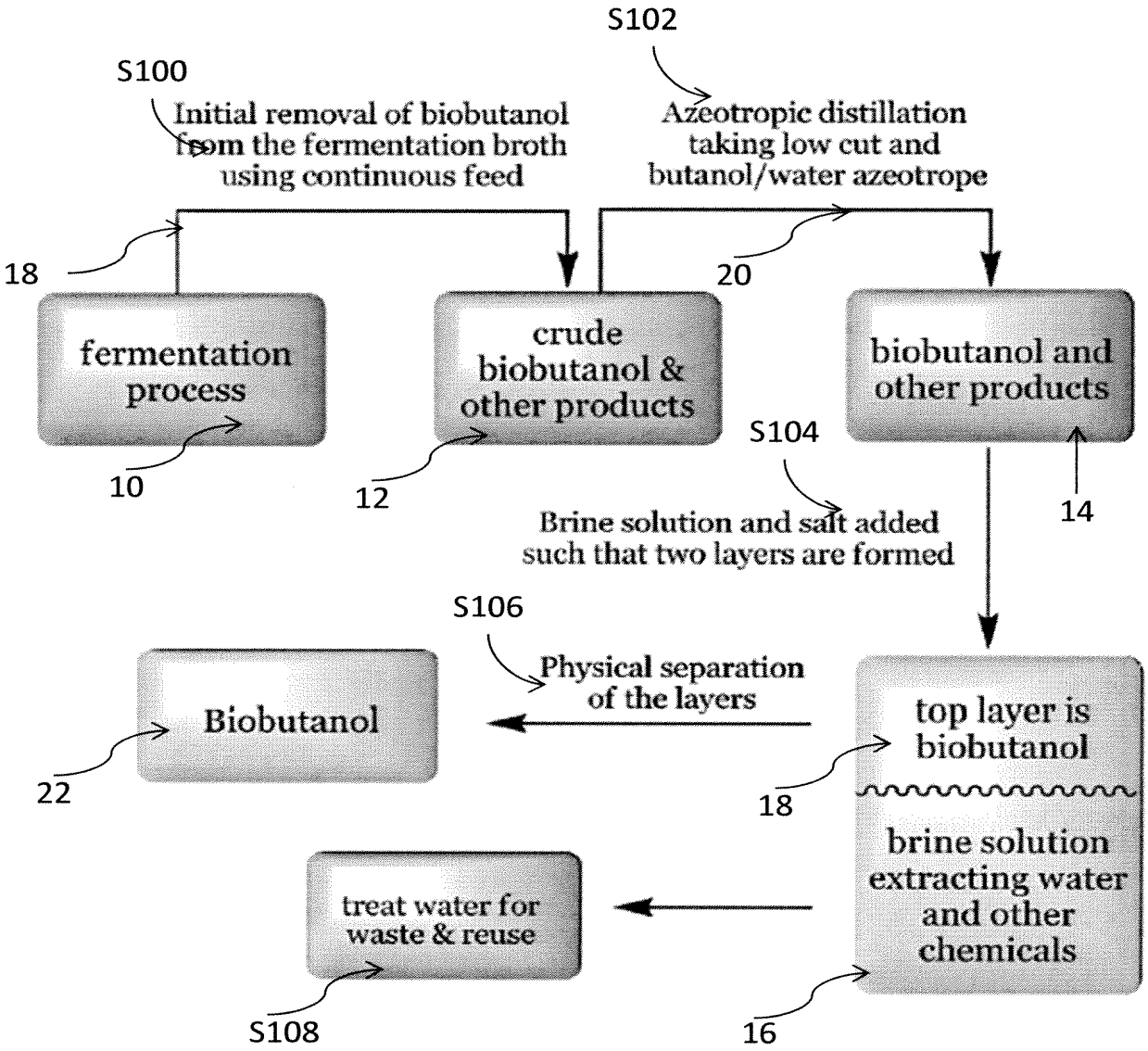
S100
Initial removal of biobutanol from the fermentation broth using continuous feed
S102
Azeotropic distillation taking low cut and butanol/water azeotrope
18
20
fermentation process
crude biobutanol & other products
biobutanol and other products
10
12
S104
14
Brine solution and salt added such that two layers are formed
S106
Physical separation of the layers
Biobutanol
top layer is biobutanol
22
18
brine solution extracting water and other chemicals
treat water for waste & reuse
S108
16

FIG. 1

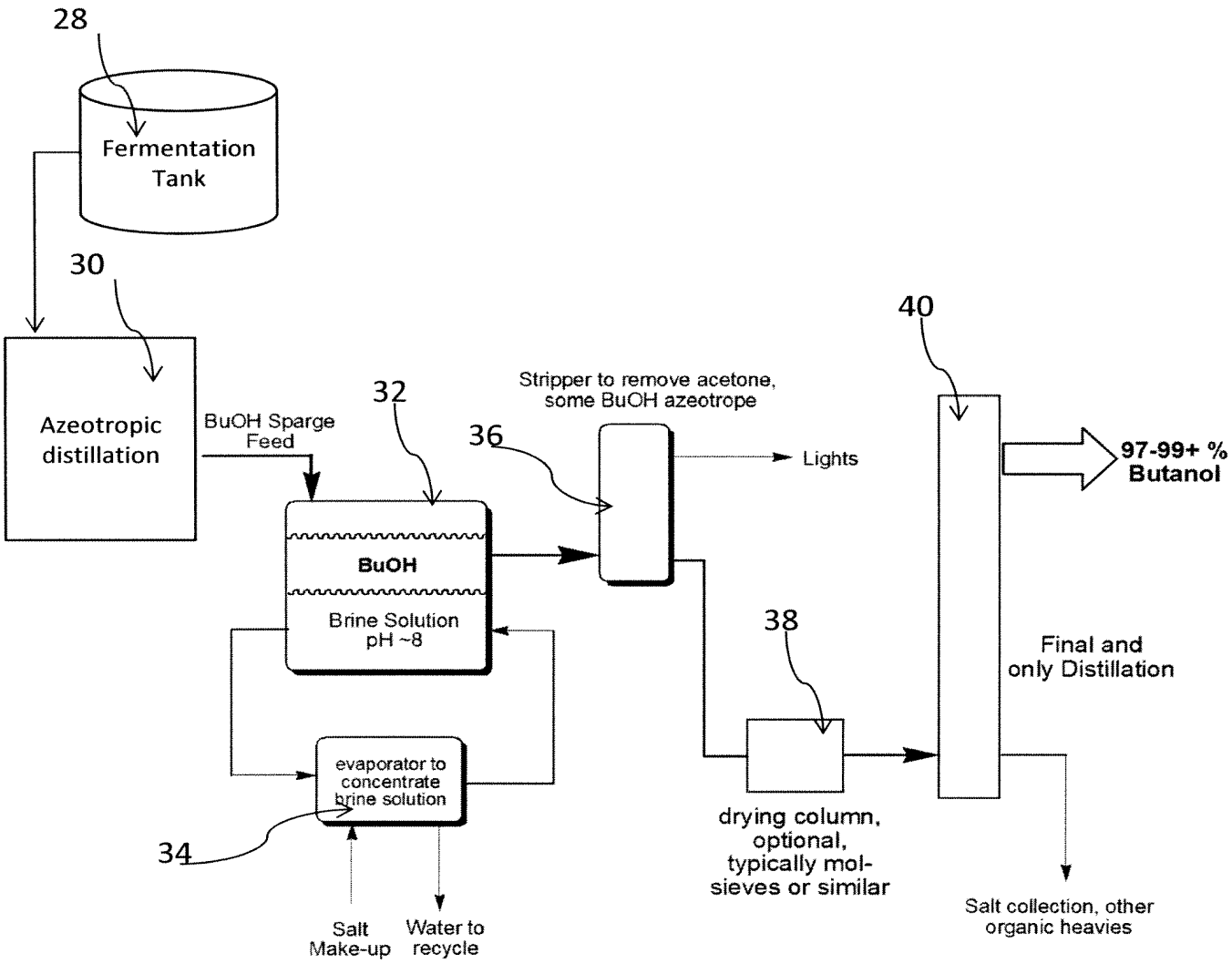
28
Fermentation Tank
30
Azeotropic distillation
BuOH Sparge Feed
32
BuOH
Brine Solution pH ~8
evaporator to concentrate brine solution
34
Salt Make-up
Water to recycle
Stripper to remove acetone, some BuOH azeotrope
36
Lights
38
drying column, optional, typically mol-sieves or similar
40
97-99+ % Butanol
Final and only Distillation
Salt collection, other organic heavies

FIG. 2

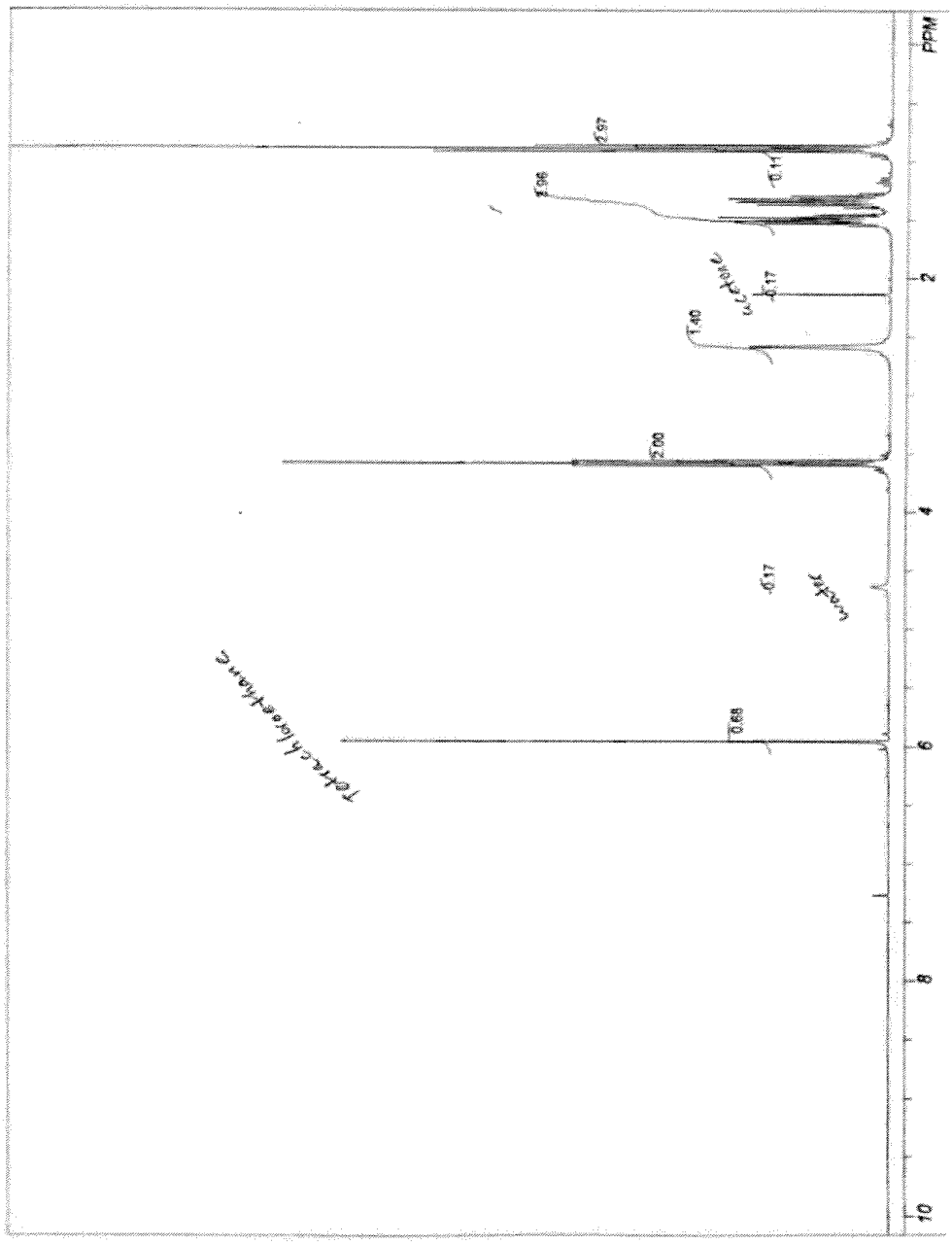

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/35132

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C12P 7/16, B01D 3/00, C02F 1/04 (2012.01)
USPC - 435/160, 210/633, 210/600
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC -- 435/160, 210/633, 210/600, 435/157, 435/155, 435/132, 435/41, 210/664, 210/188

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST -- PGPB,USPT,USOC,EPAB,JPAB; Dilaog Classic Files -- 654, 652, 349, 348, 340, 35, 65, 155; USPTO Web Page; Google Scholar; Search terms -- purification, 1-butanol, 2-butanol, fermentation broth, saturated salt, phase separation, distillation, fractionation, apparatus, dewatering, sodium chloride, brine, inert gas, sparging, membrane separat

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0132730 A1 (MANZER et al.) 05 June 2008 (05.06.2008) para [0007], [0010], [0016], [0042]-[0049], [0051], [0053], [058], [0068]-[0071], Fig 2-5	1-31, 32A, 32B, 33
Y	US 2011/0111475 A1 (KUHRY et al.) 12 May 2011 (12.05.2011) para [0013], [0019], [0045], [0048], [0057], [0087]	1-31, 32A, 32B, 33
Y	US 2010/0155333 A1 (HUSAIN et al.) 24 June 2010 (24.06.2010) para [0004], [0023], [0025], [0036]-[0038], [0046], [0048]	1-31, 32A, 32B, 33
Y	US 2008/0102502 A1 (FOODY et al.) 01 May 2008 (01.05.2008) para [0042], [0045], [0049], [0055]-[0060], [0118], [0119]	10, 19/10, 30, 32B
Y	US 4,473,444 A (FELDMAN et al.) 25 September 1984 (25.09.1984) col 4, ln 51-55; col 5, ln 34-56, Table 1	11, 14, 15, 19/(11,14,15), 25, 29
Y	US 2002/0177728 A1 (BOUDREAUX et al.) 28 November 2002 (28.11.2002) para [0051], [0053]	11, 19/11

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2012 (27.06.2012)	24 JUL 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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(54) **Title**: HOMOGENEOUS METALLOCENE ZIEGLER-NATTA CATALYSTS FOR THE OLIGOMERIZATION OF OLEFINS IN ALIPHATIC-HYDROCARBON SOLVENTS

(57) **Abstract**: A process is disclosed that permits continuous batch conversion of alpha-olefins and internal-olefins to oligomeric materials without fouling the reaction vessel and provides a simple and highly efficient method for making very cost effective catalyst systems based on Zeigler-Natta Group 4 metallocenes. Embodiments of this invention produce diesel and turbine fuels that are 100% synthetic iso-paraffinic kerosenes with flashpoints greater than 61 °C.

WO 2013/106065 A1

HOMOGENEOUS METALLOCENE ZIEGLER-NATTA CATALYSTS FOR THE OLIGOMERIZATION OF OLEFINS IN ALIPHATIC-HYDROCARBON SOLVENTS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

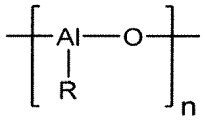
[0002] The invention generally relates to an approach that permits continuous batch conversion of alpha-olefins and internal olefins to oligomeric materials without fouling the reaction vessel and provides a simple and highly efficient method for making very cost effective catalyst systems based on Group 4 metallocenes. Embodiments of the invention create synthetic iso-paraffinic kersosenes with high flashpoints suitable for use gas, diesel, and turbine engines.

SUMMARY

[0003] A process for preparing an Activated Homogeneous Metallocene Catalyst (AHMC) includes contacting a metallocene precatalyst of the formula (I):

$$L^1L^2MX^1X^2 \qquad (I)$$

with an alkylaluminoxane of formula (II):



(II);

[0004] The precatalyst, alkylaluminoxane and/or their combination is combined with at least one saturated hydrocarbon solvent. M is Ti, Zr, or Hf. X^1 and X^2 are independently at least one of

halogen, hydrogen, alkyl, and a mixture thereof. L^1 and L^2 are independently at least one π-ligand selected from the group consisting of cyclopentadienyl, indenyl, fluorenyl, and derivatives thereof. n is an integer of at least 3. R is a C_1-C_{30} alkyl. The at least one saturated hydrocarbon solvent can be selected from the group consisting of cycloalkanes, normal alkanes, iso-alkanes, and combinations thereof.

[0005] In another aspect, a process for oligomerizing an α-olefin can be performed by contacting an olefin feedstock with the Activated Homogeneous Metallocene Catalyst to form an olefinic-oligomer product, the olefin feedstock including at least one olefin, such as an α-olefin.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] **FIG. 1** is a photograph of a beaker removed directly from SS-bomb showing a typical homogeneous oligomeric mixture from 1-butene that contains the Cp_2ZrCl_2/MAO catalyst system prepared in cyclohexane, according to embodiments of the invention.

[0007] It is to be understood that the foregoing general description and the following detailed description are exemplary and explanatory only and are not to be viewed as being restrictive of the invention, as claimed. Further advantages of this invention will be apparent after a review of the following detailed description of the disclosed embodiments, which are illustrated schematically in the accompanying drawings and in the appended claims.

DETAILED DESCRIPTION OF EMBODIMENTS OFTHE INVENTION

[0008] The invention generally relates to an approach that permits continuous batch conversion of alpha-olefin and internal-olefins to oligomeric materials without fouling the reaction vessel and provides a simple and highly efficient method for making very cost effective catalyst systems based on Group 4 metallocenes.

[0009] Currently no homogeneous Ziegler Natta (ZN) catalyst can be used in the absence of aromatic solvents. Aspects of the exemplary embodiments disclosed herein provide a versatile and inexpensive means for creating and using highly active catalysts for the oligomerization of alpha-olefins, like 1-butene. Hence, the method is very valuable for turning 1-butene (made from bio-1-butanol) to oligomers suitable for use in creating diesel and jet fuels with flashpoints over 61 deg C.

Furthermore, by addition of a homogeneous isomerization catalyst mixtures of alpha-olefins and internal-olefins can be converted to high flashpoint diesel and jet fuels using a homogeneous ZN catalyst prepared as disclosed herein. The exemplary activated catalyst can be used in oligomerization and/or dimerization of olefins in the absence of any aromatic solvents (i.e., where aromatic solvents make up less than 5 wt.% or less than 1 wt. % of the liquid reaction mixture).

[0010] In various aspects, an activated catalyst, a method for making it and a method for using it to oligomerize/dimerize an olefin are disclosed.

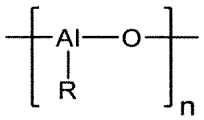
[0011] One aspect of the invention includes a fuel(s). The fuel(s) can be produced from oligomerization and/or dimerization processes including at least one alpha-olefin and/or internal olefins, at least one homogenous Ziegler-Natta catalyst and at least one homogenous activating co-catalyst (e.g., together forming the exemplary activated catalyst), and at least one or mixture hydrocarbon solvent, where the fuel has a flashpoint of 61 to 100 °C. Embodiments of the invention further include at least one olefin-isomerization catalyst. Other embodiments of the invention include the Ziegler-Natta catalyst being group four (4) metallocene catalyst. In other embodiments, the co-catalyst is an alkylaluminoxane (AAO). Yet in other embodiments, the catalyst is prepared by contacting a metallocene precatalyst with an aliphatic hydrocarbon solution containing an alkylaluminoxane (AAO). In still yet other embodiments, the aliphatic hydrocarbon solution is derived from a fuel.

[0012] Embodiments of the invention include the activated catalyst being prepared by dissolving trialkylalane in an aliphatic-hydrocarbon solvent (e.g., a fuel) and being treated with one mol-equivalent of water and then contacted with a metallocene precatalyst and filtered. In embodiments, the trialkylalanes are selected from the group consisting of trimethylalane, triethylalane, tributylalane, and tri(iso-butyl)alane (TIBA). In other embodiments, the aliphatic hydrocarbon solvents (which can be fuels) are selected from the group consisting of straight chain alkanes including hexane, heptane, octane, nonane, decane, and alkanes having greater than 10 carbons. In yet other embodiments, the aliphatic hydrocarbon solvents are C6 to C16 hydrocarbons and may be selected from the group consisting of, but not limited to, branched-aliphatic-hydrocarbons including 3-methylheptane, 2-methyloctane, and the like. Still yet in other embodiments, the aliphatic hydrocarbon solvents are selected from the group consisting of, but not limited to, cyclic aliphatic-hydrocarbons including cyclohexanes, methylcyclohexanes,

dimethylcyclohexanes, tetralins, pinanes, and other mono- and bicyclic aliphatic-hydrocarbons.

[0013] Another aspect of the invention includes a process for preparing a saturated hydrocarbon fuel including contacting an olefin feedstock with an Activated Homogeneous Metallocene Catalyst (AHMC) for use in the dimerization and oligomerization of olefins, such as neat α-olefins, where the AHMC can be prepared by contacting a metallocene precatalyst of the formula (I) with an alkylaluminoxane of formula (II), where the latter is prepared in and/or the resulting activated catalyst mixed with a saturated hydrocarbon solvent:

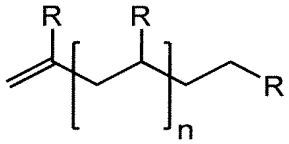
$$L^1L^2MX^1X^2 \qquad (I)$$



(II)

[0014] In formula ((I), M is Ti, Zr, or Hf, X^1 and X^2 is at least one halogen, hydrogen, alkyl, or a mixture thereof, L^1 and L^2 are comprised of π-ligands selected from the group consisting of cyclopentadienyl, indenyl, fluorenyl and derivatives thereof. In the derivatives, substituents are attached to the ligands, the attachments includes ansa-linkages that bind the two rings, with at least one carbon or silicon atoms each bearing hydrogen or alkyl radicals. In formula (II), n is an integer of at least 3, and R can be a C_1-C_{30} alkyl, which can be linear, branched, or a combination thereof. The at least one saturated hydrocarbon solvent can be selected from the group consisting of cycloalkanes, normal-alkanes, and/or iso-alkanes.

[0015] The Al/M molar ratio can be about 1 to 100. In other embodiments, the Al/M molar ratio is 10 to 20. Embodiments of the invention include the product being prepared by placing the activated catalyst in contact with a neat solution having at least one α-olefin during a period of 1 to 24 h and forms the α-olefinic-oligomer (III) in 98-100% conversion based on starting α-olefins:



(III)

[0016] In formula (III) each R can be independently as described for formula (II).

[0017] Embodiments of the invention include the AHMC being introduced in one portion, in discrete aliquots, or through a continual addition process directly to the neat (undiluted) α-olefin

feedstock. Embodiments of the invention include the ratio of metallocene precatalyst (g of M) to α-olefinic-oligomer product (Kg) being about 5 to 40. In other embodiments, the entire α-olefinic-oligomer product (III) is transferred to quench vessel, treated with water, and then filtered to remove solids. In other embodiments, the α-olefinic-oligomer product (III) is passed through an alumina or other metal oxide filter material to remove M and Al species from the product solution. Other embodiments, the α-olefinic-oligomer product (III) is treated with a stabilizing agent selected from either a hydroquinone or phenol family of stabilizers, e.g., with butylated hydroxytoluene (BHT) and at concentrations of 10-300 ppm.

[0018] Embodiments of the invention include the process lowering the boiling fraction of the α-olefinic-oligomer products (III) between 50 °C and 150 °C, including between 70 °C and 130 °C, and are removed by flash distillation. Embodiments of the invention include the process having a low boiling fraction from about 25 to 45 wt. % of the total α-olefinic-oligomer product, or comprises about 30-40 wt. % of the total α-olefinic-oligomer. In embodiments, the process includes a light boiling fraction subjected to selective-dimerization chemistries to create a mixture of mono-olefinic hydrocarbon products having a boiling point greater than 200 °C but less than 300 °C at atmospheric pressure. Embodiments of the invention include the process having a high boiling fraction subjected to catalytic hydrogenation over heterogeneous metal catalysts having palladium, platinum, and/or nickel (or any combination thereof). Embodiments of the invention include the process having a hydrogen pressure in the range of about 30-3000 psig (approximately 300-20800 kpa), or a pressure between 50 and 100 psig (approximately 440-790 kpa). Embodiments of the invention the reaction temperature used is in the range of about 20 to 100 °C with ambient or 40 °C temperature range.

[0019] Embodiments of the invention further include the product being subjected to hydrogenation over heterogeneous metal catalysts which includes palladium, platinum, and/or nickel; hydrogen pressure is performed in the range of about 30-3000 psig, or a pressure between 1000 and 2000 psig. In embodiments, the temperature is in the range of 20 to 100 °C or 60 °C to 80 °C temperature range. In embodiments, the products are combined and distilled at atmospheric pressure. In other embodiments, the products obtained are combined and distilled at reduced pressure. Embodiments of the invention a collection of hydrocarbon, a completely 100% synthetic iso-paraffinic kerosene (SiPK) product, starting at 150 °C and finishing at 280 °C affords a fuel

mixture that meets Jet-A/JP-8 and diesel #1 flashpoint requirements (≥38 °C). Embodiments of the invention the SiPK jet/diesel fuel produced has a derived Cetane index of 40-55 or 50 Cetane index. In other embodiments, the SiPK jet/diesl fuel produced has a maximum cold flow viscosity of 8 cSt as measured at -20 °C (ASTM 445LT).

[0020] Embodiments of the invention include the collection of product starting at 170 °C and finishing at 280 °C yields a SiPK jet/diesel that meets military JP-5 and diesel #2 flashpoint requirements with a flashpoint >61 °C. Embodiments of the invention include the SiPK jet/diesel fuel produced has a derived Cetane index of 40-55 or 50 Cetane index. Embodiments of the invention include SiPK jet/diesl fuel produced has a maximum cold flow viscosity of 8.5 cSt as measured at -20 °C (ASTM 445LT).

[0021] The α-olefins can be selected from the group consisting of, but not limited to, 1-propene, 1-butene, 1-pentene, and 1-hexene, with neat 1-butene or a mixture of 1-butene and 1-propene (3:1, mol:mol, respectively).

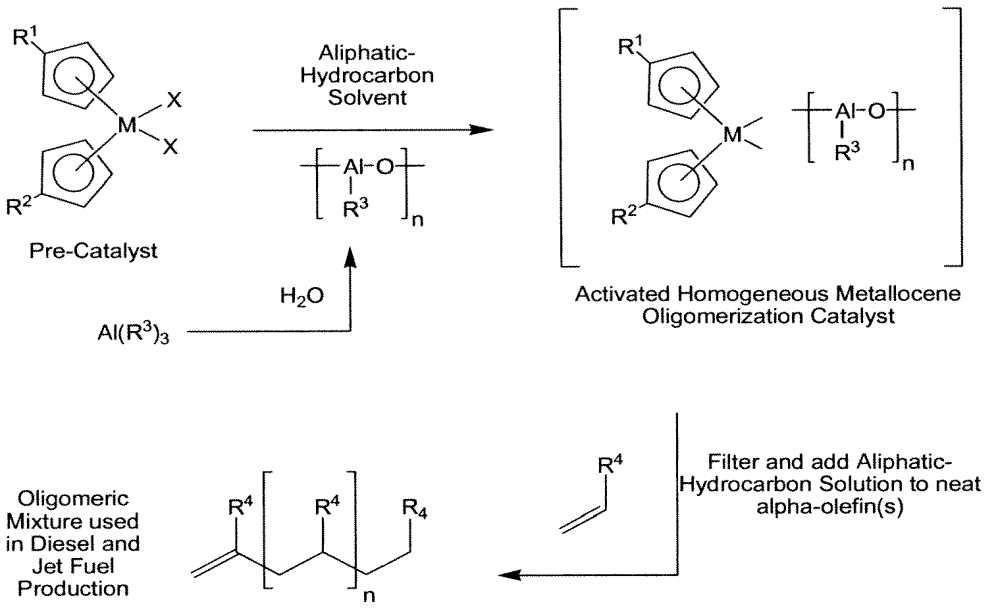
[0022] In embodiments of the invention the π-ligands can be cyclopentadienyl, R is methyl, and the aliphatic hydrocarbon solvent is cyclohexane or methylcyclohexane. Embodiments of the inventions include the π-ligands are cyclopentadienyl rings having at least one alkyl group attached, R is methyl, and the aliphatic hydrocarbon solvent is selected from the group consisting of cyclic, acyclic linear and branched hydrocarbon solvent that include jet and diesel fuels prepared. Embodiments of the invention include the π-ligands being cyclopentadienyl, R is at least three carbons, and the aliphatic hydrocarbon solvent is selected from acyclic linear and/or branched hydrocarbon solvent.

[0023] Embodiments of the invention include the trialkylalane compound being prepared by direct reaction of one mole of trialkylalane with one mole-equivalent of water in an SiPK. Other embodiments of the invention include the trialkylalane is selected from the group consisting of, but not limited to, trimethyl, triethylalane, tripropylalane, tri-isopropylalane, tributylalane, and tri-isobutylalane, and tri-isobutylalane. Still yet in other embodiments the π-ligands are cyclopentadienyl rings having at least two alkyl groups attached, R is methyl, and the aliphatic hydrocarbon solvent is selected from the group consisting of cyclic, acyclic linear, branched hydrocarbon solvents, solutions thereof, and jet and diesel fuels previously prepared. Embodiments of the invention include a fuel having a flashpoint of about 61 to about 100. Embodiments of the

invention further include an isomerization catalyst having a range from about 0.1 ppm to about 0.1 weight %, relative to the total olefin component.

[0024] Oligomers, suitable for conversion and use as jet and diesel fuels, are prepared from alpha-olefins using highly active purely homogeneous Ziegler-Natta catalysts, a homogeneous co-catalyst, and in pure aliphatic hydrocarbon solvent. The oligomerization can be conducted controlled without the use of hydrogen and produce an ideal molecular distribution of oligomers for use in preparing diesel and jet fuels. This method creates fuels that do not require any subsequent hydrocracking or reforming yet retain outstanding cold flow properties and exceptionally high gravimetric densities.

[0025] The homogeneous catalyst of embodiments of the invention is prepared as shown in Scheme 1 by contacting a metallocene precatalyst with a solution of an alkylaluminoxane (AAO). Typically, R^1 and R^2 can independently be hydrogen or any combination of C_1-C_{30} alkyl chains. The R^1 and R^2 substituents(s) are linear or branched chains and/or a combination thereof. The alkylaluminoxane can be prepared using methods that are familiar to people skilled in the art, e.g., from a trialkylalane $Al(R_3)_3$ where R^3 is typically a C_1-C_{30} alkyl group, although larger chains can be employed. Branching in the alkyl group can be used to increase solubility although is not required herein. When the AAO is prepared in an aromatic solvent, the metallocene precatalyst is combined and the aromatic solvent is removed under reduced pressure and the solids redissolved in the desired aliphatic-hydrocarbon solvent or fuel, filtered if necessary, and then transferred to the reaction vessel that contains the mixture of alpha-olefin and internal-olefins. These activated homogeneous catalyst solutions are stable and suitable for storage. Typical alpha-olefins can include R^4 being a C_1-C_{10} alkyl group that can be a linear chain or contain branching at various places in the carbon chain. The internal olefin is any olefin-isomer where the double-bond has chemically migrated internally along the carbon chain. The homogeneous isomerization catalyst takes the internal-olefin and isomerizes the bond so as to create the corresponding alpha-olefin.

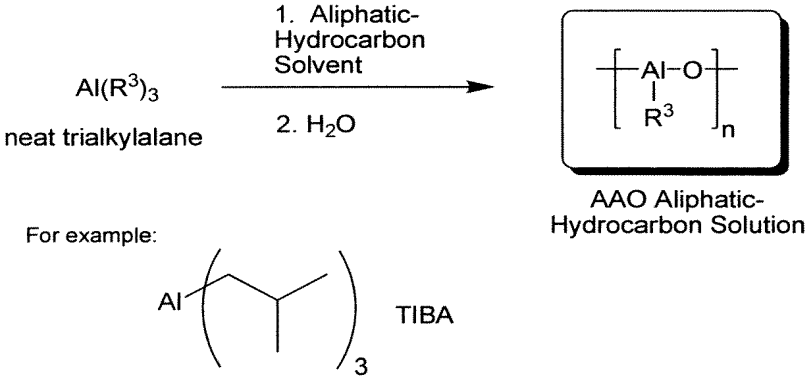


Scheme 1

[0026] Another embodiment of the chemical process for preparing the homogeneous metallocene catalyst in pure aliphatic-hydrocarbon solvent is illustrated in Scheme 2: A trialkylalane is dissolved in an aliphatic-hydrocarbon solvent and treated with one mol-equivalent of water, this solution is then placed in contact with a metallocene precatalyst. The molar ratio of alane/metallocene can be varied from 1:1 to 100:1, respectively, depending on the desired catalytic process and outcome. The final solutions may be filtered to remove any impurities or undesired products resulting from the controlled hydrolysis of the alane and subsequent reaction with the metallocene pre-catalyst. The final solutions are typically light yellow in color and crystal clear to the eye. Typical concentrations of the active homogeneous catalysts are in the range of 0.1M to 0.01M, with lower concentrations possible with equal catalytic activity. These latter solutions can be stored for long periods or immediately transferred to reaction vessels using common techniques that include Teflon® diaphragm pumps or by simple polypropylene syringes, all with equal success and retention of catalyst activity.

[0027] Typical trialkylalanes can be trimethylalane, triethylalane, tripropylalane, tributylalane, and tri(isobutyl)alane (TIBA), which are all commercially available. Alanes containing longer alkyl

chains can be prepared by existing methods familiar to those in the art by simple reaction of an alkyl Grignard with aluminum trichloride. For the methylaluminoxane, toluene solutions can be utilized from commercial sources to prepare the active metallocene catalyst followed by removal and recycling of the toluene. Then the active metallocene/MAO catalyst can be dissolved in the desired aliphatic-hydrocarbon solvent. Use of MAO in this invention it is found preferable to utilize a metallocene precatalyst that has alkyl substitution on one or more of the cyclopentadienyl rings, although this is not required if certain aliphatic hydrocarbon solvents are used. In general, alkyl-substitution of the metallocene rings provides enhanced solubility over a range of aliphatic-hydrocarbons and can be used to increase the activated metallocene catalyst concentration when desired.



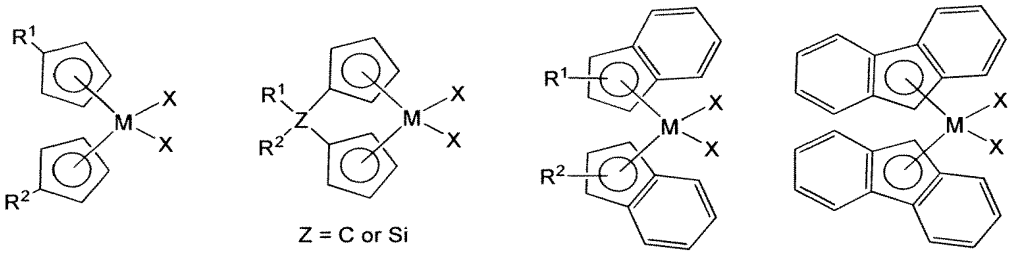
Scheme 2

[0028] Typical aliphatic-hydrocarbon solvents useful in this invention include straight chain alkanes such as hexane, heptanes, octane, nonane, and decane. Branched-aliphatic-hydrocarbons such as 3-methylheptane, 2-methylheptane, and 2-methyloctane work well in this invention as well as other branched aliphatic hydrocarbons containing from 6 to 16 carbons. In particular, C12 to C16 staturated synthetic iso-paraffinic kerosenes are suitable for use in this embodiment. Cyclic aliphatic-hydrocarbons can be used that include cyclohexane, methylcyclohexane, dimethylcyclohexanes, tetralin, pinane, and other mono- and bicyclic aliphatic-hydrocarbons.

[0029] Useful metallocene pre-catalysts for this invention can be prepared by several methods, some found in the open literature covering nearly four decades of group metallocene synthetic

procedures [Y. Qian et al., *Chem. Rev.,* 103(7), pp 2633-2690 (2003); R. Halterman, *Chem. Rev.,* 92(5), pp 965-994 (1992)]. In addition, two patents describe the synthesis of simple bis(n-alkylcyclopentadienyl)MCl_2 (where M = Group 4 transition metal) [J.-S. Oh et al. US6214953 B1 (2001) and J. M. Sullivan et al. US6175027 B1 (2001)]. Oh and co-workers describe the use of alkyl-metallocenes for preparing supported ZN-catalysts and Sullivan and coworkers do not report any catalytic chemistry or solubility properties for the metallocene compounds prepared.

[0030] By way of example, unsubstituted and all alkyl and multiple-alkyl substituted metallocenes, ansa-metallocenes, indenyl, fluorocenyl, and related metallocenes can be used in the present invention when combined with the appropriate aliphatic-hydrocarbon solvent and AAO, all affording highly active and selective oligomerization ZN-catalysts. Examples of the precatalyst (I) include formulas (IV)-(VII) below.



(IV) (V) (VI0) (VII)

[0031] Olefinic monomers that can be used in the current invention include α-olefins (including ethane), mono- and bicyclic olefins, dienes, vinyl-aromatics and the like. Examples include ethene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, cyclopentene, cyclopentadiene, norbornene, styrene, and the like. The olefin monomer can be copolymerized with one or more other monomers. Internal-olefins including 2-hexene, 2-pentene, 2-butene can be used in the invention by introduction of a homogeneous group 8 transition metal complex/isomerization catalyst, with nickel being another embodiment of a transition metal.

EXAMPLE 1: Preparation of the Homogeneous Zn-Catalyst in an Aliphatic-Hydrocarbon Solvent

[0032] A Schlenk flask is charged with Cp_2ZrCl_2 (0.080 g, 0.274 mmol) and 10 mL of a toluene MAO solution (8.0 wt. % active MAO). Cp=cyclopentadiene. The toluene was removed

under reduced pressure to afford a yellow solid. To this mixture was added cyclohexane (15 mL) and heated briefly with stirring to dissolve the activated catalyst. The solution was allowed to settle and clear yellow solution was collected by syringe (~10 mL) and used directly or stored for future use.

EXAMPLE 2: Oligomerization of an Alpha-Olefin Using a Homogeneous ZN-Catalyst Delivered in an Aliphatic Hydrocarbon-Solvent

[0033] 1-Butene (~390 g, ~ 500 mL, CP grade) was condensed over calcium hydride inside a Schlenk flask maintained at -70 °C and re-evaporated and passed through a column of activated alumina in route to being condensed inside a dried 0.7L capacity PARR SS bomb. A 500 mL beaker was placed inside the bomb to simulate a glass lined reaction vessel. Once the 1-butene was condensed inside the SS bomb the sample was subjected to five evacuation/backfill cycles to remove residual amounts of oxygen. The homogeneous aliphatic-hydrocarbon solution containing the active catalyst was added to the mixture and 3 addition evacuation/backfill cycles were performed. The SS bomb was sealed and allowed to react for 8 h. Shorter times could be used if the SS bomb was warmed by external heat. Typically after ~1 h the bomb reached a maximum pressure of 80 psig and approached 60 °C in temperature. At completion of the reaction little or no pressure remained in the vessel and the when removed from the SS bomb the beaker contained a clear light yellow solution of oligomers (see Figure 1). Quenching the mixture with 0.5 mL of water and then drying over potassium carbonate (~3 g) afforded ~380 g of an oligomeric mixture suitable for use in making diesel and jet fuels with flash points over 61 deg C.

[0034] **Figure 1** shows a beaker removed directly from SS-bomb showing a typical homogeneous oligomeric mixture from 1-butene that contains the Cp_2ZrCl_2/MAO catalyst system prepared in cyclohexane. The sample contains no aromatic hydrocarbons. It is a clear solution.

[0035] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both

limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

CLAIMS

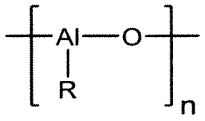
What is Claimed is:

1. A process for preparing an Activated Homogeneous Metallocene Catalyst (AHMC) suited for use in the dimerization and oligomerization of α-olefins, comprising:

contacting a metallocene precatalyst of the formula (I):

$L^1L^2MX^1X^2$ (I)

with an alkylaluminoxane of formula (II):



(II); and

at least one of the precatalyst, the alkylaluminoxane, and their combination being combined with at least one saturated hydrocarbon solvent,

wherein:

M is Ti, Zr, or Hf;

X^1 and X^2 are independently at least one of halogen, hydrogen, alkyl, and a mixture thereof;

L^1 and L^2 independently comprise at least one π-ligand selected from the group consisting of cyclopentadienyl, indenyl, fluorenyl, and derivatives thereof,

n is an integer of at least 3;

R comprises a C_1-C_{30} alkyl; and

the at least one saturated hydrocarbon solvent optionally being selected from the group consisting of cycloalkanes, normal alkanes, iso-alkanes, and combinations thereof.

2. The process according to claim 1, further characterized by combining the precatalyst with the at least one saturated hydrocarbon solvent prior to contacting it with the alkylaluminoxane.

3. The process according to claim 1, further characterized by said π-ligand being a derivative of cyclopentadienyl, indenyl, or fluorenyl, and wherein substituents are attached to said ligands through ansa-linkages that bind the respective rings, with at least one carbon or silicon atom, each bearing hydrogen or alkyl radicals.

4. The process according to claim 1, further characterized by R being a linear or branched alkyl, or a combination thereof.

5. The process according to claim 1, further characterized by the contacting including an Al/M molar ratio of from 1 to 100.

6. The process according to claim 5, further characterized by said Al/M molar ratio being from 10 to 20.

7. A process for oligomerizing an olefin characterized by:

contacting an olefin feedstock with the Activated Homogeneous Metallocene Catalyst prepared according to the process of any one of claims 1-6 to form an olefinic-oligomer product, the olefin feedstock comprising at least one olefin,

the olefin optionally comprising an α-olefin.

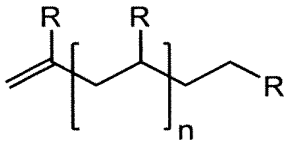
8. The process of claim 7, further characterized by the olefin feedstock comprising less than 20 wt. %, or less than 10 wt. % or less than 5 wt. % or less than 1 wt. % of all constituents other than the at least one olefin.

9. The process of claim 7, further characterized by the contacting including contacting the olefin feedstock for at least one hour.

10. The process of claim 7, further characterized by the olefin comprising an α-olefin and the contacting forming an α-olefinic-oligomer in at least a 98% conversion.

11. The process of claim 7, further characterized by the olefin comprising an α-olefin

and the contacting forming an α-olefinic-oligomer of according to formula (III):



(III)

12. The process according to claim 7, further characterized by said AHMC being introduced in one portion, in discrete aliquots, or through a continual addition process directly to the olefin feedstock.

13. The process according to claim 7, further characterized by a ratio of metallocene precatalyst (g of M) to α-olefinic-oligomer product (Kg) being from 5 to 40.

14. The process according to claim 7, further characterized by transferring said olefinic-oligomer product to a quench vessel, treated with water, and then filtered to remove solids.

15. The process according to claim 7, further characterized by passing said olefinic-oligomer product through metal oxide filter material to remove M and Al species from said product solution.

16. The process according to claim 15, further characterized by the metal oxide comprising alumina.

17. The process according to claim 7, further characterized by treating said olefinic-oligomer product with a stabilizing agent selected from a hydroquinone or phenol family of stabilizers, optionally with butylated hydroxyl toluene (BHT), at a concentration of 10-300 ppm.

18. The process according to claim 7, further characterized by removing, by flash distillation, a lower boiling fraction of the olefinic-oligomer products.

19. The process according to claim 7, further characterized by removing a lower boiling fraction of α-olefinic-oligomer products between 50 °C and 150 °C, or between 70 °C and 130 °C.

20. The process according to claim 18 or 19, further characterized by said lower boiling fraction being from 25 to 45 wt. % of the total α-olefinic-oligomer product, or 30-40 wt. % of the total α-olefinic-oligomer product.

21. The process according to claim 7, further characterized by subjecting a light boiling fraction of said α -olefinic-oligomer product to selective-dimerization to create a mixture of mono-olefinic hydrocarbon products having a boiling point greater than 200 °C but less than 300 °C at atmospheric pressure.

22. The process according to claim 7, further characterized by subjecting a high boiling fraction of said α-olefinic-oligomer product to catalytic hydrogenation over at least one heterogeneous metal catalyst comprising at least one of palladium, platinum, and nickel.

23. The process according to claim 22, further characterized by said subjecting being performed at a hydrogen pressure in the range of 300-20800 kpa, or between 440 and790 kpa.

24. The process according to claim 22, further characterized by said subjecting being performed at a temperature in the range of 20 to 100 °C, or at 20-50°C, or at 35-45°C, or at 60-80°C.

25. The process according to claim 22, further characterized by said product being subjected to hydrogenation over a heterogeneous metal catalyst which comprises at least one of palladium, platinum, and nickel and hydrogen pressure in the range of 300-20800 kpa, or a pressure between 7000 and 14000 kpa.

26. The process according to claim 25, further characterized by said products being combined and distilled at atmospheric pressure.

27. The process according to claim 25, further characterized by said products obtained being combined and distilled at reduced pressure.

28. The process according to claim 26, further characterized by collecting a hydrocarbon product, a completely 100% synthetic iso-paraffinic kerosene (SiPK) product, starting at 150 °C and finishing at 280 °C, suitable as a jet/diesel fuel.

29. The process according to claim 26, further characterized by the product collected providing a fuel mixture that meets Jet-A/JP-8 and diesel #1 flashpoint requirements (≥38 °C).

30. The process according to claim 28 or 29, further characterized by said SiPK jet/diesel fuel produced having a derived Cetane index of 40-55, or a Cetane index of 50.

31. The process according to claim 28 or 29, further characterized by said SiPK jet/diesel fuel produced having a maximum cold flow viscosity of 8 cSt as measured at -20 °C (ASTM 445LT).

32. The process according to claim 26, further characterized by collecting a product starting at 170 °C and finishing at 280 °C which yields a SiPK jet/diesel that meets military JP-5 and diesel #2 flashpoint requirements with a flashpoint >61 °C.

33. The process according to claim 32, further characterized by said SiPK jet/diesel fuel produced having a derived Cetane index of 40-55 or 50 Cetane index.

34. The process according to claim 32 or 33, further characterized by said SiPK jet/diesel fuel produced having a maximum cold flow viscosity of 8.5 cSt as measured at -20 °C (ASTM 445LT).

35. The process according to claim 7, further characterized by said olefin feedstock comprising an α-olefin selected from the group consisting of 1-propene, 1-butene, 1-pentene, 1-hexene, and combinations thereof.

36. The process according to claim 35, further characterized by said α-olefin being neat 1-butene or a mixture of 1-butene and 1-propene, optionally at a ratio of 1-butene to 1-propene of 3:1, mol:mol.

37. The process according to claim 7, further characterized by the contacting being performed in the absence of aromatic solvents.

38. A fuel produced by the method of any one of claims 7-19, 21-29, 32-33, and 35-37.

39. The process according to claim 1, further characterized by said aliphatic hydrocarbon solvent is a cycloaliphatic hydrocarbon.

40. The process according to claim 1, further characterized by said π-ligands are cyclopentadienyl, R is methyl, and said aliphatic hydrocarbon solvent is at least one of cyclohexane and methylcyclohexane.

41. The process according to claim 1, further characterized by said π-ligands are cyclopentadienyl rings having at least one alkyl group attached, R is methyl, and the aliphatic hydrocarbon solvent is selected from the group consisting of cyclic, acyclic linear and branched hydrocarbon solvents that include jet and diesel fuels.

42. The process according to claim 1, further characterized by said π-ligands are cyclopentadienyl, R is at least three carbons, and the aliphatic hydrocarbon solvent is selected from acyclic linear and/or branched hydrocarbon solutions and fuels.

43. The process according to claim 1, further characterized by said alkylaluminoxane being prepared by direct reaction of one mole of trialkylalane with one mol-equivalent of water in iso-paraffinic kerosene.

44. The process according to claim 43, further characterized by said trialkylalane

being selected from the group consisting of trimethylalane, triethylalane, tripropylalane, tri-isopropylalane, tributylalane, tri-isobutylalane, tri-isobutylalane and combinations thereof.

45. The process according to claim 1, further characterized by said π-ligands are cyclopentadienyl rings having at least two alkyl groups attached, R is methyl, and the aliphatic hydrocarbon solvent is selected from the group consisting of cyclic, acyclic linear, branched hydrocarbon solvent, and jet and diesel fuels prepared.

46. The process according to claim 1, further characterized by said solvent being a fuel having a flashpoint of at least 61, or 61- 100.

47. The process according to claim 1, further characterized by an isomerization catalyst at from 0.1 ppm to 0.1 weight %, relative to the total olefin component.

48. An Activated Homogeneous Metallocene Catalyst produced by the process of any one of claims 1-6 and 39-47.

49. A process for forming a fuel, comprising:

providing an olefin feedstock comprising at least of an one alpha-olefin and an internal olefin;

combining the olefin feedstock with a catalyst comprising at least one homogenous Ziegler-Natta catalyst and at least one homogenous activating co-catalyst, and at least one hydrocarbon solvent to form the fuel by at least one of oligomerization and dimerization.

50. The process according to claim 49, further characterized by the combining being performed in the absence of any aromatic solvents.

51. The process according to claim 49, further characterized by at least one olefin-isomerization catalyst.

52. The process according to claim 49, further characterized by said Ziegler-Natta

catalyst including a group four (4) metallocene catalyst.

53. The process according to claim 49, wherein said co-catalyst is an alkylaluminoxane (AAO).

54. The process according to claim 49, further characterized by said catalyst being prepared by contacting a metallocene precatalyst with an aliphatic hydrocarbon solution having an alkylaluminoxane (AAO).

55. The process according to claim 49, further characterized by said aliphatic hydrocarbon solvent being derived from a fuel.

56. The process according to claim 49, further characterized by said catalyst being prepared by dissolving a trialkylalane in an aliphatic-hydrocarbon solvent and/or fuel and treating it with one mol-equivalent of water, which is then contacted with a metallocene precatalyst and filtered.

57. The process according to claim 55, further characterized by said trialkylalanes being selected from the group consisting of trimethylalane, triethylalane, tributylalane, and tri(iso-butyl)alane (TIBA).

58. The process according to claim 55, further characterized by said aliphatic hydrocarbon solvents and/or fuels being selected from the group consisting of straight chain alkanes including hexanes, heptanes, octanes, nonanes, decanes, and alkanes having greater than 10 carbons.

59. The process according to claim 55, further characterized by said aliphatic hydrocarbon solvents and/or fuels being selected from the group consisting of branched-aliphatic-hydrocarbons of 6 to 16 carbons.

60. The process according to claim 59, further characterized by said branched-

aliphatic-hydrocarbon being selected from the group consisting of 3-methylheptane, 2-methyloctane, and combinations thereof.

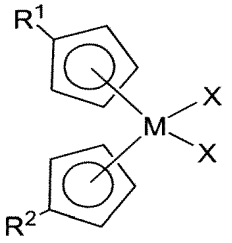
61. The process according to claim 55, further characterized by said aliphatic hydrocarbon solvents and/or fuels being selected from the group consisting of cyclic aliphatic-hydrocarbons including cyclohexanes, methylcyclohexanes, dimethylcyclohexanes, tetralins, pinanes, and other mono- and bicyclic aliphatic-hydrocarbons.

62. The process according to claim 49, further characterized by said fuel having a flashpoint of 61 to 100 °C.

63. A fuel prepared by the process of any one of claims 49-62.

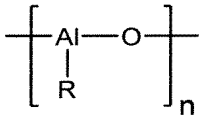
64. A process for oligomerizing an olefin characterized by:

a) contacting a metallocene precatalyst of the formula (I):



(I)

with an alkylaluminoxane of formula (II):



(II);

the precatalyst contacted with the alkylaluminoxane being combined with at least one saturated hydrocarbon solvent to provide an Activated Homogeneous Metallocene Catalyst,

wherein:

M is Ti, Zr, or Hf;

X^1 and X^2 are independently at least one of halogen, hydrogen, alkyl, and a mixture thereof;

R comprises a C_1-C_{30} alkyl;

R^1 and R^2 are independently comprise a C_1-C_{30} alkyl or H,

n is an integer of at least 3;

; and

the at least one saturated hydrocarbon solvent is selected from the group consisting of cycloalkanes, normal alkanes, iso-alkanes, and combinations thereof; and

b) contacting an olefin feedstock with the Activated Homogeneous Metallocene Catalyst form an olefinic-oligomer product, the olefin feedstock comprising at least one olefin.

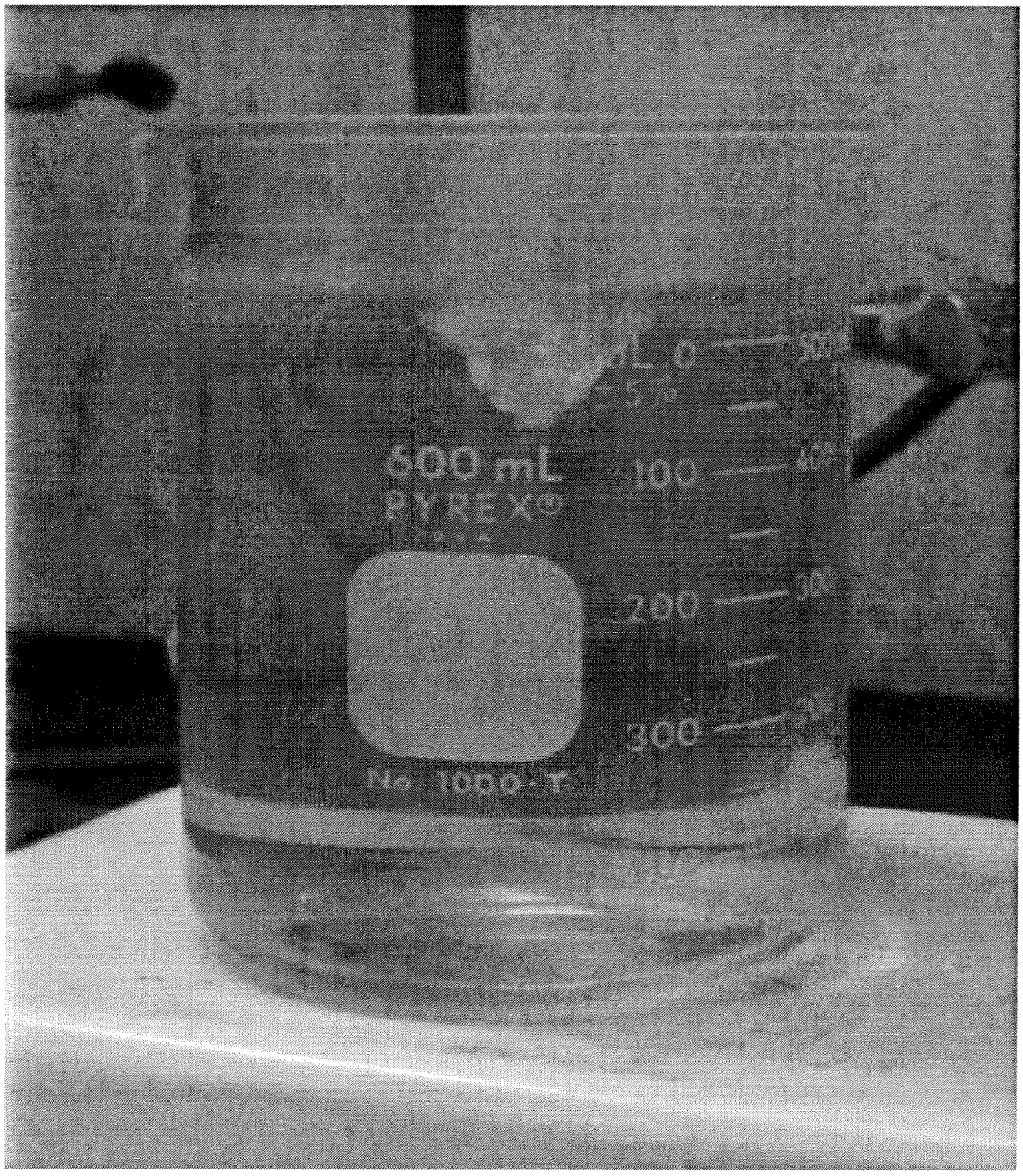


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/35167

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01J 31/00; B01J 37/00 (2012.01)
USPC - 502/104
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) -B01J 31/00; B01J 37/00 (2012.01)
USPC -502/104

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 502/118, 152; 526/160, 165, 943 (see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST, Google Patents, Google Scholar, WIPO (Metallocene, precatalyst, catalyst, process, formula, aluminoxane, olefin, homogeneous, aluminoxane, ligand, kerosene, Ziegler, quench, flash, point, oligomer, activated, alkylaluminoxane, fuel, solvent, diesel, metal, oxide, alumina, dimerization, filter, medium, internal, natta, co-catalyst

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 2007/0293640 A1 (JIANG, et al.) 20 December 2007 (20.12.2007) entire document, especially para[0007], [0020], [0038]-[0041], [0058], [0096], [0112]-[0113], [0122], [0128], [0135], [0141]-[0144], [0162], [0219], [0246]-[0250], [0255], [0260]-[0263], [0266]-[0267], [0962], [0977], [1038], [1070], [1187], [1189].	1-14,19,20/19,35-37, 39-40,42,47,48/(1-6,39-42, 47), 64 ---------- 15-18, 20/18, 21-34, 41, 43-46, 48/(41,43-46), 49-63
Y	US 2007/0185362 A1 (LATTNER, et al.) 09 August 2007 (09.08.2007) entire document, especially para[003], [0344], [0354].	15-16, 18, 20/18
Y	US 5,158,992 A (CASSELLI, et al.) 27 October 1992 (27.10.1992) entire document, especially col 1, ln 54-56; col 5, ln 52-55.	17 21
Y	US 2007/0293712 A1 (TITTA, et al.) 20 December 2007 (20.12.2007) entire document, especially para[0033], [0044].	22-34
Y	US 2011/0114538 A1 (COSYNS, et al.) 19 May 2011 (19.05.2011) entire document, especially para[0050]-[0051], [0054], [0058], [0126].	31-34, 41, 45-46, 48/(41,45-46), 49-62, 63/(49-62)
Y	US 2009/0305926 A1 (WU, et al.) 10 December 2009 (10.12.2009) entire document, especial para[0001], [0004], [0007]-[0008], [0018]-[0019], [0029], [0035], [0050]-[0051], [0072], [0090], [0126].	43-44, 48/(43-44), 56-57, 63/(56-57)
Y	US 4,772,736 A (EDWARDS, et al.) 20 September 1988 (20.09.1988) entire document, especially col 1, ln 27-col 2, ln 2.	

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 August 2012 (05.08.2012)	14 AUG 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/35167

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 38
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)

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C07C 1/24(2006.01)

(56)对比文件
Behrooz Fallah等.A New Nano-(2Li2O/MgO) Catalyst/Porous Alpha-Alumina Composite for the Oxidative Coupling of Methane Reaction.《AIChE Journal》.2009,第56卷(第3期),第717-728页.

审查员 程远梅

权利要求书1页 说明书5页

(54)发明名称

C6～C10醇脱水制备相应碳数烯烃的催化剂

(57)摘要

本发明涉及C_6～C_{10}醇脱水制备相应碳数烯烃的催化剂，C_6～C_{10}醇脱水制备相应碳数烯烃方法，主要解决现有技术中存在脱水催化剂稳定性差的问题，本发明通过采用C_6～C_{10}醇脱水制备相应碳数烯烃的催化剂，所述催化剂以重量份数计，包括以下组份：a)0.01～30份的IA或ⅡA中的金属氧化物至少其中之一；b)70～99.99份的Al_2O_3；所述金属氧化物与Al_2O_3的份数之和为100份的技术方案，较好地解决了该技术问题，可用于C_6～C_{10}醇脱水制备相应碳数烯烃工业生产中。

CN 105312044 B

1.C_6～C_{10}醇脱水制备相应碳数烯烃的方法，包括在所述催化剂存在下使所述醇或所述醇的含水混合物为反应原料进行脱水反应生成所述相应碳数烯烃；

所述催化剂以重量份数计，包括以下组份：

a)0.01～30份的金属氧化物，所述金属氧化物为Li_2O和MgO；

b)70～99.99份的Al_2O_3；

所述金属氧化物与Al_2O_3的份数之和为100份。

2.根据权利要求1所述的方法，其中，以重量份数计，所述金属氧化物的用量为0.05～20份，Al_2O_3的用量为80～99.95份。

3.根据权利要求2所述的方法，其中，以重量份数计，所述金属氧化物的用量为0.1～15份，Al_2O_3的用量为85～99.9份。

4.根据权利要求1所述的方法，其中，所述的醇为1-辛醇，所述的相应碳数烯烃为1-辛烯。

5.根据权利要求1或4所述的方法，其中，所述醇的含水混合物中醇的重量百分浓度为≥5%且＜100%。

6.根据权利要求1或4所述的方法，其中，反应温度为200～500℃。

7.根据权利要求1或4所述的方法，其中，以醇计反应原料体积空速为0.1～25小时$^{-1}$。

8.根据权利要求1或4所述的方法，其中，所述催化剂的制备方法包括以下步骤：将所需量的选自拟薄水铝石、薄水铝石、三水铝石或湃耳石中的至少一种、含Li和含Mg的化合物、助挤剂和胶溶剂混合，成型，然后干燥、焙烧，得到所述催化剂。

C_6～C_{10}醇脱水制备相应碳数烯烃的催化剂

技术领域

[0001] 本发明涉及C_6～C_{10}醇脱水制备相应碳数烯烃的催化剂，C_6～C_{10}醇脱水制备相应碳数烯烃方法，尤其涉及1-辛醇脱水制备1-辛烯的方法。

背景技术

[0002] 正辛烷是无色透明液体，不溶于水，溶于乙醇、乙醚、苯、丙酮等多数有机溶剂，主要用作高档溶剂和有机合成。

[0003] 正辛烷的可以从相关石油馏分分离得到，由于石油馏分组份复杂，难以获得纯度高的产品。

[0004] 辛醇脱水制辛烯一般采用改性的氧化铝催化剂。

[0005] 黄晴等发表的论文〔2-辛醇气相脱水合成2-辛烯，工业催化，2007年3月，第15 卷，第3期，P50-53〕报道，在330℃，0.35h^{-1}空速下，600小时稳定性试验中2-辛烯收率最高达到93%，但是稳定性不理想，600小时收率降低至75%。

[0006] 高占先等发表等论文〔改性氧化铝催化伯醇脱水合成1-烯烃研究，大连理工大学学报，2001年7月，第41卷，第4期，P412-415〕报道，通过对氧化铝催化剂改性，340℃、常压下，辛醇转化率达到96.8%，辛烯选择性约为70%，未见稳定性情况。

[0007] 辛醇脱水，一般同时存在双键转移现象，产品中主要有1-，2-，3-双键辛烯。在制取正辛烷情况下，这些异构体都可以加氢成为目的产物正辛烷。因此，也可以使用价格较低的混合辛醇原料经过催化脱水制辛烯。

[0008] 1-辛醇脱水制备1-辛烯，1-辛烯加氢制得正辛烷可以获得高纯度正辛烷产品。辛烯加氢可以使用工业上常用的催化剂如Raney Ni，负载Ni，负载Pd，负载Pt催化剂。

[0009] 综上所述，以往技术中采用的脱水催化剂，存在催化剂稳定性差的缺点。

发明内容

[0010] 本发明所要解决的技术问题之一是现有技术中存在脱水催化剂稳定性差的问题，提供一种C_6～C_{10}醇脱水制备相应碳数烯烃的催化剂。该催化剂具有稳定性好的特点。

[0011] 本发明所要解决的技术问题之二是提供采用上述技术问题之一所述的催化剂的C_6～C_{10}醇脱水制备相应碳数烯烃的方法。

[0012] 为解决上述技术问题之一，本发明的技术方案如下：C_6～C_{10}醇脱水制备相应碳数烯烃的催化剂，所述催化剂以重量份数计，包括以下组份：

[0013] a)0.01～30份的ⅠA或ⅡA中的金属氧化物至少其中之一；

[0014] b)70～99.99份的Al_2O_3；

[0015] 所述金属氧化物与Al_2O_3的份数之和为100份。

[0016] 上述技术方案中，以重量份数计，ⅠA或ⅡA中的金属氧化物的用量优选为0.05～20份，Al_2O_3的用量优选为80～99.95份；更进一步，以重量份数计，ⅠA或ⅡA中的金属氧化物的用量更优选为0.1～15份，Al_2O_3的用量更优选为85～99.9份。

[0017] 上述技术方案中，IA金属氧化物优选自Li_2O，ⅡA金属氧化物优选自MgO。所述催化剂更优选同时包括Li_2O和MgO。

[0018] 为解决上述技术问题之二，本发明的技术方案如下：C_6～C_{10}醇脱水制备相应碳数烯烃的方法，包括在上述技术问题之一的技术方案中任一项所述催化剂存在下使所述醇或所述醇的含水混合物为反应原料进行脱水反应生成所述相应碳数烯烃。

[0019] 上述技术方案中，所述的醇优选为1-辛醇，所述的相应碳数烯烃优选为1-辛烯。

[0020] 上述技术方案中，所述醇的含水混合物中醇的重量百分浓度优选为≥5%且＜100%。

[0021] 上述技术方案中，反应温度优选为200～500℃，更优选为200～450℃，进一步优选为 250～450℃。

[0022] 上述技术方案中，以醇计反应原料体积空速优选为0.1～25小时$^{-1}$，更优选为0.5～20 小时$^{-1}$，进一步优选为0.5～15小时$^{-1}$。

[0023] 上述技术方案中，所述催化剂的制备方法没有特别限制，所述催化剂的优选制备方法包括以下步骤：将所需量的选自拟薄水铝石、薄水铝石、三水铝石或湃耳石中的至少一种、含IA或ⅡA中至少一种金属的化合物、助挤剂和胶溶剂混合，成型，然后干燥、焙烧，得到所述催化剂。

[0024] 所述助挤剂优选方案为选自田菁粉、甘油、石墨、干淀粉或柠檬酸中至少一种。所述胶溶剂优选方案为选自硝酸、柠檬酸、乙二酸或乙酸中的至少一种。所述含IA或ⅡA 金属化合物可以是无机或者有机化合物，但以可以在较高温度下分解而不残留其他离子为适宜，优选方案为选自硝酸盐或乙酸盐中的至少一种。

[0025] 本发明中催化剂的寿命判断依据是经过相同时间反应后，通过差热分析得到催化剂的积碳总量，再经过计算，得到单位时间催化剂的积碳百分比量，即积碳速率(单位：%/小时)。该积碳速率越大，催化剂对应的失活速率就越快，催化剂的寿命就越短。

[0026] 本发明通过添加IA或ⅡA中至少一种金属氧化物，用于C_6～C_{10}醇脱水制备相应碳数烯烃过程时，催化剂的积碳速率与氧化铝相比，大幅度降低了积碳速率，从而使得催化剂具有较好的稳定性和寿命。例如通过同比，在用于1-辛醇脱水制1-辛烯时，本发明催化剂的积碳速率可抵达0.0351%/小时，1-辛醇转化率高达99.53%，1-辛烯选择性高达 98.76%，而氧化铝的积碳速率同比高达0.0874%/小时，1-辛醇转化率高达95.24%，1-辛烯选择性高达93.83，取得了较好的技术效果，可用于C_6～C_{10}醇脱水制备相应碳数烯烃工业生产中。

[0027] 下面通过实施例对本发明作进一步阐述。

具体实施方式

[0028] 【实施例1】

[0029] 称量拟薄水铝石200克于捏合机中，加入2克田菁粉捏合30分钟，滴加0.5w%乙酸锂水溶液60毫升，再加200毫升0.5w%硝酸水溶液捏合30分钟，挤条成型，于120℃烘干12小时，550℃焙烧10小时，即得长为5毫米直径为3毫米催化剂催化剂A。催化剂中Al_2O_3的重量份数为99.95份，Li_2O重量份数为0.05份。为便于比较，将催化剂的组成列于表1。

[0030] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱

仪分别分析。反应条件及反应结果见表2。

[0031] 【实施例2】

[0032] 称量拟薄水铝石200克于捏合机中，加入2克甘油捏合30分钟，滴加20w％乙酸锂水溶液60毫升，再加200毫升0.5w％柠檬酸水溶液捏合30分钟，挤条成型，于150℃烘干10小时，700℃焙烧5小时，即得长为5毫米直径为3毫米催化剂B。催化剂中Al_2O_3的重量份数为98.08份，Li_2O重量份数为1.92份。为便于比较，将催化剂的组成列于表 1。

[0033] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0034] 【实施例3】

[0035] 称量拟薄水铝石200克于捏合机中，加入2克石墨捏合30分钟，滴加15w％乙酸锂水溶液10毫升，再加200毫升0.5w％乙二酸水溶液捏合30分钟，挤条成型，于140℃烘干10小时，650℃焙烧15小时，即得长为5毫米直径为3毫米催化剂C。催化剂中 Al_2O_3的重量份数为99.76份，Li_2O重量份数为0.24份。为便于比较，将催化剂的组成列于表1。

[0036] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0037] 【实施例4】

[0038] 称量拟薄水铝石200克于捏合机中，加入2克田菁粉捏合30分钟，滴加15w％硝酸锂水溶液50毫升，再加200毫升0.5w％硝酸水溶液捏合30分钟，挤条成型，于120℃烘干12小时，550℃焙烧10小时，即得长为5毫米直径为3毫米催化剂D。催化剂中 Al_2O_3的重量份数为98.85份，Li_2O重量份数为1.15份。为便于比较，将催化剂的组成列于表1。

[0039] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0040] 【实施例5】

[0041] 称量薄水铝石200克于捏合机中，加入2克田菁粉捏合30分钟，滴加15w％硝酸锂水溶液40毫升，再加200毫升0.5w％硝酸水溶液捏合30分钟，挤条成型，于90℃烘干 20小时，500℃焙烧20小时，即得长为5毫米直径为3毫米催化剂E。催化剂中Al_2O_3的重量份数为99.12份，Li_2O重量份数为0.88份。为便于比较，将催化剂的组成列于表 1。

[0042] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0043] 【实施例6】

[0044] 称量薄水铝石200克于捏合机中，加入2克干淀粉捏合30分钟，滴加15w％硝酸锂水溶液40毫升，再加200毫升1.5w％柠檬酸水溶液捏合30分钟，挤条成型，于120℃烘干12小时，600℃焙烧10小时，即得长为5毫米直径为3毫米催化剂F。催化剂中Al_2O_3的重量份数为99.61份，Li_2O重量份数为0.39份。为便于比较，将催化剂的组成列于表 1。

[0045] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂

装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0046] 【实施例7】

[0047] 称量三水铝石200克于捏合机中，加入3克石墨捏合30分钟，滴加15w％硝酸锂水溶液40毫升，再加200毫升1w％乙二酸水溶液捏合30分钟，挤条成型，于100℃烘干 15小时，700℃焙烧5小时，即得长为5毫米直径为3毫米催化剂G。催化剂中Al_2O_3的重量份数为98.83份，Li_2O重量份数为1.17份。为便于比较，将催化剂的组成列于表 1。

[0048] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0049] 【实施例8】

[0050] 同【实施例7】，只是采用硝酸镁。

[0051] 称量三水铝石200克于捏合机中，加入3克石墨捏合30分钟，滴加10w％硝酸镁水溶液48.4毫升，再加200毫升1w％乙二酸水溶液捏合30分钟，挤条成型，于100℃烘干15小时，700℃焙烧5小时，即得长为5毫米直径为3毫米催化剂为H。催化剂中Al_2O_3的重量份数为98.83份，MgO重量份数为1.17份。为便于比较，将催化剂的组成列于表 1。

[0052] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0053] 【实施例9】

[0054] 称量三水铝石200克于捏合机中，加入3克石墨捏合30分钟，滴加15w％硝酸锂水溶液20毫升和10w％硝酸镁水溶液24毫升，再加200毫升1w％乙二酸水溶液捏合30 分钟，挤条成型，于100℃烘干15小时，700℃焙烧5小时，即得长为5毫米直径为3 毫米催化剂I。催化剂中Al_2O_3的重量份数为98.83份，Li_2O重量份数为0.59份，MgO 重量份为0.58份。为便于比较，将催化剂的组成列于表1。

[0055] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0056] 【对比例1】

[0057] 称量拟薄水铝石200克于捏合机中，加入2.5克干淀粉捏合30分钟，加200毫升0.5w％硝酸水溶液捏合30分钟，挤条成型，于120℃烘干12小时，550℃焙烧10小时，即得长为5毫米直径为3毫米催化剂J。催化剂中Al_2O_3的重量份数为100份。为便于比较，将催化剂的组成列于表1。

[0058] 催化剂的性能评价在固定床管式反应器(Φ25×500毫米不锈钢)上进行，催化剂装载量为10毫升，反应时间为100小时。反应产物经气液分离后采用Agilent4890气相色谱仪分别分析。反应条件及反应结果见表2。

[0059] 表1催化剂组成(重量份)

[0060]

	Al_2O_3	Li_2O	MgO

实施例1	99.95	0.05	
实施例2	98.08	1.92	
实施例3	99.76	0.24	
实施例4	98.85	1.15	
实施例5	99.12	0.88	
实施例6	99.61	0.39	
实施例7	98.83	1.17	
实施例8	98.83		1.17
实施例9	98.83	0.59	0.58
对比例1	100		

[0061] 表2

[0062]

	原料	温度 ℃	空速 小时$^{-1}$	辛醇 转化率%	辛烯 选择性%	积碳速率 %/小时
实施例1	辛醇	330	0.8	100.00	97.82	0.0380
实施例2	35%辛醇	300	0.5	100.00	98.23	0.0419
实施例3	25%辛醇	290	5	99.99	97.19	0.0454
实施例4	45%辛醇	260	12	98.00	97.25	0.0370
实施例5	85%辛醇	280	1	99.96	97.32	0.0400
实施例6	50%辛醇	400	10	99.98	97.03	0.0410
实施例7	75%辛醇	270	6	98.79	98.36	0.0392
实施例8	75%辛醇	270	6	98.92	98.24	0.0382
实施例9	75%辛醇	270	6	99.53	98.76	0.0351
对比例1	75%辛醇	270	6	95.24	93.83	0.0874

[0063] 注:表2中辛醇为1-辛醇;表中原料中辛醇前的百分数表示原料为辛醇和水混合物的情况下原料中辛醇的重量百分比浓度;辛烯为1-辛烯。

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Optimized assignee	CHINA PETROLEUM & CHEMICAL CORP. INC.	Strategic Importance	2.77
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Bibliography

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Catalyst used in dehydrogenation of alcohol for producing olefin, comprises specified amount of specified group metal oxide and alumina

Original Title

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English Title

Assignee/Applicant

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CN201410353875A / 2014-07-24

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CN201410353875A / 2014-07-24 / CN

DWPI Priority number / Date / Country code

Abstract

Abstract

The invention relates to C6~C10 alcohol dehydration catalyst for preparing corresponding carbon number olefin, C6~C10 alcohol dewatering method preparing corresponding carbon number olefin, mainly solving the problem that the dehydration catalyst stability is bad. The invention uses C6~C10 alcohol dehydration catalyst for preparing corresponding carbon number olefin, the catalyst based on parts by weight, comprising the following components: a) at least one of 0.01~30 parts of I A or II A in the metal oxide, b) 70~99.99 parts of Al2O3; said metal oxide to Al2O3 parts and 100 parts of the technical plan better solves the problem, can be used for C6~C10 alcohol dehydration to prepare corresponding carbon number olefin in industrial production.

(Translation from Clarivate Analytics)

Classes/Indexing

IPC

Current IPC	Invention	Version	Additional	Version
Full	B01J 23/04 B01J 21/10 C07C 1/24 C07C 11/02	20060101 20060101 20060101 20060101	-	-
Main Group	-	-	-	-
Subclass	-	-	-	-

Original IPC	Invention	Version	Additional	Version
Advanced/Full	B01J 23/04 B01J 21/10 C07C 11/02 C07C 1/24	20060101 20060101 20060101 20060101	-	-
Core/Main Group	-	-	-	-

Subclass	-	-	-	-

DWPI manual codes

Expand DWPI manual codes

Legal status

Predictive Analytics

Predictive Type	Data
Probability of Grant	100.00
Probability of Early Lapse	11.80
Probability of Restoration Post-Lapse	-

INPADOC Legal Status

Gazette Date	Code	Description
2018-02-13	GR01 +	PATENT GRANT
2016-03-09	C10	ENTRY INTO SUBSTANTIVE EXAMINATION
2016-02-10	C06 +	PUBLICATION

Get Family Legal Status

Family

Family

INPADOC Family (2) **INPADOC family:** Alive

	Publication number	Publication date	Inventor	Assignee/Applicant	Dead/Alive	Title
	CN105312044B	2018-02-13	JIN Zhao-sheng	Sinopec Corp.		C6～C10醇脱水制备相应碳数烯烃的催化剂
	CN105312044A	2016-02-10	JIN Zhao-sheng	CHINA PETROLEUM & CHEMICAL		Catalyst used for preparing olefin with corresponding carbon number via C6-C10 alcohol dehydration

Claims

Claims

All Claims (8)

Claims (English)

1.C6~C10 alcohol dehydration method, comprising for preparing corresponding carbon number olefin in the presence of the catalyst the aqueous mixture of the alcohol or the alcohol as reaction raw material to dehydration reaction to generate the respective carbon numbers of olefins, the catalyst based on parts by weight. it comprises the following components: a) 0.01~30 parts of metal oxide, the metal oxide is Li2O and MgO, b) 70~99.99 parts of Al2O3, Al2O3 parts of the metal oxide and is 100 parts.

2. The method according to claim 1, wherein, by weight, the dosage of said metal oxide is 0.05~20 parts; the dosage of the Al2O3 is 80~99.95 parts.

3. The method according to claim 2, wherein, by weight, the dosage of said metal oxide is 0.1~15 parts; the dosage of the Al2O3 is 85~99.9 parts.

4. The method according to claim 1, wherein said alcohol is 1-octanol, the corresponding carbon number olefin is 1-octylene.

5. The method according to claim 1 or 4, wherein the weight percentage concentration of the alcohol in the aqueous mixture of the alcohol is more than or equal to 5% and <100 %.

6. The method according to claim 1 or 4, wherein the reaction temperature is 200~500 degrees centigrade.

7. The method according to claim 1 or 4, wherein alcohol reaction raw material volume space velocity is 0.1~25 -1.

8. The method according to claim 1 or 4, wherein the preparation method of the catalyst comprises the following steps: the required amount selected from pseudo-boehmite, boehmite, trihydrate aluminium or Enpai-Otolith at least one of the compound containing, extrusion assistant

and peptizing agent of Li and Mg-containing mixing, moulding, and then drying, roasting to obtain the catalyst.
(Translation from Clarivate Analytics)

Description

Background/ Summary

Background/Summary

Drawing description

Drawing Description

Description

Description

the technical field

The invention relates to C6~C10 alcohol dehydration catalyst for preparing corresponding carbon number olefin, C6~C10 alcohol dewatering method preparing corresponding carbon number olefin, especially 1-octanol dehydration preparation method of 1-octylene.

the background technology

octane is colourless transparent liquid, insoluble in water, soluble in many organic solvent of ethanol, aether, benzene, acetone and so on, mainly used as solvent and organic synthesis.

octane can be separated from associated petroleum fractions obtained, the petroleum fraction component is complex, it is difficult to obtain the high purity of the product.

octanol octene generally uses the modified alumina catalyst.

such as published thesis [2-octanol phase dehydration industrial catalysis, synthesizing 2-octylene, 2007 December 3, 15 roll, 3, P50-53 report, at 330 degrees centigrade, 0.35h-1 air speed 600-hour stability test in 2-octylene yield up to 93%, but stability is not ideal, 600 yield is reduced to 75%.

high pre-emptive published thesis modified-alumina catalytic primary alcohol synthetized by dehydration of 1-olefin research, Dalian University of Technology Journal, December 2001, 7, coil 41, first 4, P412-415 report, by modifying the alumina catalyst, 340 degrees centigrade under the normal pressure, octanol conversion rate reaches 96.8%, the octene selectivity is about 70%, there is no stability condition.

octanol, double bond transfer phenomenon generally exist at the same time, the product is mainly with 1 -, 2 -, 3-double bond octene. under the condition of producing octane, these isomers can be hydrogenated to form target product octane. Therefore, it also can use the mixed raw material with lower price through catalytic dehydrating octene.

1-octanol is dehydrated to prepare 1-octylene, 1-octene hydrogenation octane can obtain high purity n-octane product. octene hydrogenation using a catalyst such as Raney Ni, load Ni, Pd load common in industry, supported Pt catalyst.

In summary, in the prior art the dehydration catalyst, catalyst stability is poor.

invention content

The invention solves the technical problem in the existing technology has bad dehydration catalyst stability problem, to provide a C6~C10 alcohol dehydration catalyst for preparing corresponding carbon number olefins. The catalyst has good stability.

the second technical problem to be solved by the present invention is to provide uses C6~C10 alcohol above technical problem of the catalyst dehydration method of preparing corresponding carbon number olefins.

In order to solve said technical problem, the technical solution of the invention is as follows: C6~C10 alcohol dehydration catalyst for preparing corresponding carbon number olefin, the catalyst based on parts by weight, comprising the following components:

at least one of a) 0.01~30 parts of I A or II A in the metal oxide;

b) 70~99.99 parts of Al2O3;

the metal oxide and Al2O3 parts and 100 parts.

In the technical solution, preferably in an amount of 0.05~20 parts of metal oxide by weight, I A or II A, the dosage of Al2O3 is preferably 80~99.95, further, the dosage of metal oxide by weight, I A or II A is more preferably 0.1~15, more preferably 85~99.9 of dosage of the Al2O3.

In the technical solution, I A metal oxide is preferably selected from Li2O, metal oxide is preferably selected from MgO. the catalyst more preferably comprises Li2O and MgO.

In order to solve said technical problem, the technical solution of the invention is as follows: C6~C10 alcohol dehydration to prepare corresponding carbon number olefins, comprising one of said technical problem the technical solution of any one of the aqueous mixture of the catalyst in the presence of the alcohol or the alcohol as reaction raw material to dehydration reaction to generate the respective carbon numbers of olefins.

In the technical solution, the alcohol is preferably octanol, the corresponding carbon number olefin preferably 1-octene.

In the technical solution, the weight percentage concentration of the alcohol water mixture of said alcohol is preferably equal to 5% and <100 %.

In the technical solution, the reaction temperature is preferably 200~500 degrees centigrade, more preferably 200~450 degrees centigrade, more preferably 250~450 degrees centigrade.

the technical solution in the alcohol reaction volume airspeed of the raw material is preferably 0.1~25 to -1, more preferably 0.5~20 -1, further preferably 0.5~15 to -1.

In the technical solution, the preparation method of the catalyst is not particularly limited, the preferable preparation method of the catalyst comprises the following steps: the required amount selected from pseudo-boehmite, boehmite, trihydrate aluminium or Enpai-Otolith at least one of the containing compound, extrusion assistant and peptizing agent of at least one metal of I A or II A in mixing, moulding, and then drying, roasting to obtain the catalyst.

the extrusion solution preferably is selected from sesbania powder, glycerol, graphite, dry starch or citric acid in at least one kind of. the glue solvent solution is preferably selected from nitric acid, citric acid, at least one oxalic acid or acetic acid. the I A or II A metal compound can be inorganic or organic compounds, but can decompose without leaving other ion is suitable at the higher temperature, the preferable solution is selected from nitrate or acetate of at least one.

judging the life of catalyst according to the invention, after the same time reaction to obtain the catalyst by differential thermal analysis of the carbon amount, and then calculating the percentage amount of unit time to obtain carbon catalyst, namely carbon rate (unit: % per hour). the deposition rate is larger, the deactivation rate catalyst corresponding to the faster, life of the catalyst becomes short.

The invention is added with at least one metal oxide I A or II A in C6~C10 alcohol dehydration for preparing corresponding carbon number olefin process, the deposition rate of the catalyst compared with alumina, which greatly reduces the deposition rate, so that the catalyst has good stability and life. for example, by comparing, used in 1-octanol by dehydrating 1-octylene, the deposition rate of the catalyst of the invention can reach 0.0351%/h, 1-octanol conversion is up to 99.53%, 1-octene selectivity 98.76%, and the deposit rate of alumina up to 0.0874%/hour, 1-octanol conversion as high as 95.24%, as high as 93.83 1-octene selectivity, has good technical effect, can be used for C6~C10 alcohol dehydration to prepare corresponding carbon number olefin in industrial production.

under the present invention is further illustrated by the examples.

Specific execution examples

" embodiment 1 "

weighing 200 of pseudo-boehmite in kneader, adding 2 powder and kneading for 30, dropping 0.5w 60 % acetate water solution, then adding 200 0.5w % nitric acid aqueous solution for 30 minutes, extruding and moulding, roasting for 10 hours at 120 degrees centigrade, drying for 12 hours at 550 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst A. Al2O3 in the catalyst by weight, 99.95 parts of Li2O by weight is 0.05 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 2 "

weighing 200 of pseudo-boehmite in kneader, kneading for 30 adding 2 of glycerol, adding 20w % acetate aqueous solution 60, then adding 200 0.5w % of citric acid aqueous solution for 30 minutes, extruding and forming, roasting for 5 hours at 150 degrees centigrade, drying for 10 hours at 700 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst B. Al2O3 in the catalyst by weight, 98.08 parts of Li2O by weight is 1.92 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 3 "

weighing 200 of pseudo-boehmite in kneader, kneading for 30 adding 2 of graphite, 15w dropping 10 % acetate water solution, then adding 200 0.5w % oxalic aqueous solution and kneading for 30, extruding and forming, roasting for 15 hours at 140 degrees centigrade, drying for 10 hours at 650 degrees centigrade to obtain the length of 5 diameter is 3 catalyst. Al2O3 in the catalyst by weight, 99.76 parts of Li2O by weight is 0.24 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 4 "

weighing 200 of pseudo-boehmite in kneader, adding 2 powder and kneading for 30, dropping 15w 50 % nitrate water solution, then adding 200 0.5w % nitric acid aqueous solution for 30 minutes, extruding and moulding, roasting for 10 hours at 120 degrees centigrade, drying for 12 hours at 550 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst D. Al2O3 in the catalyst by weight, 98.85 parts of Li2O by weight is 1.15 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and

reaction result are shown in table 2.

" embodiment 5 "

weighing 200 of boehmite in the kneader, adding 2 powder and kneading for 30, dropping 15w 40 % nitrate water solution, then adding 200 0.5w % nitric acid aqueous solution for 30 minutes, extruding and moulding, roasting for 20 hours at 90 degrees centigrade, drying for 20 hours at 500 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst E. Al2O3 in the catalyst by weight, 99.12 parts of Li2O by weight is 0.88 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 6 "

weighing 200 of boehmite in kneader, kneading for 30 adding 2 of dry starch, adding 15w % 40 nitrate solution, then adding 200 1.5w % of citric acid aqueous solution for 30 minutes, extruding and forming, roasting for 10 hours at 120 degrees centigrade, drying for 12 hours at 600 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst F. Al2O3 in the catalyst by weight, 99.61 parts of Li2O by weight is 0.39 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 7 "

weighing 200 of gibbsite in kneader, kneading for 30 adding 3 of graphite, 15w dropping 40 % nitrate water solution, then adding 200 1w % oxalic aqueous solution and kneading for 30, extruding and forming, roasting for 5 hours at 100 degrees centigrade, drying for 15 hours at 700 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst G. Al2O3 in the catalyst by weight, 98.83 parts of Li2O by weight is 1.17 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 8 "

with the " embodiment 7 ", only uses magnesium nitrate.

weighing 200 of gibbsite in kneader, kneading for 30 adding 3 of graphite, dropping 10w % magnesium nitrate water solution 48.4, then adding 200 1w % oxalic aqueous solution and kneading for 30, extruding and forming, roasting for 5 hours at 100 degrees centigrade, drying for 15 hours at 700 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst H. Al2O3 in the catalyst by weight is 98.83 parts, MgO 1.17 shares of weight. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

" embodiment 9 "

weighing 200 of gibbsite in kneader, kneading for 30 adding 3 of graphite, adding 15w % nitrate water solution and 20 of 10w wt % magnesium nitrate water solution 24, then adding 200 1w % oxalic aqueous solution and kneading for 30, extruding and forming, roasting for 5 hours at 100 degrees centigrade, drying for 15 hours at 700 degrees centigrade to obtain length of 5 diameter is 3 mm. the catalyst I. Al2O3 in the catalyst by weight, 98.83 parts of Li2O by weight, 0.59 parts of MgO by weight part is 0.58 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

"Comparative Example 1"

weighing 200 of pseudo-boehmite in kneader, kneading for 30 adding 2.5 of dry starch, adding 200 0.5w % nitric acid aqueous solution for 30 minutes, extruding and moulding, roasting for 10 hours at 120 degrees centigrade, drying for 12 hours at 550 degrees centigrade to obtain the length of 5 diameter is 3 mm. the catalyst. Al2O3 in the catalyst by weight is 100 parts. to facilitate comparison, the composition of the catalyst are listed in Table 1.

the performance evaluation of the catalyst on the fixed bed tubular reactor (ϕ 25 * 500 stainless steel), catalyst loading amount is 10, the reaction time is 100 hours. the reaction product after gas-liquid separation using Agilent4890 gas-phase chromatograph analysis. reaction condition and reaction result are shown in table 2.

Table 1 catalyst composition (parts by weight)

Al2O3Li2OMgO Example 199.950.05 Example 298.081.92 Example 399.760.24 Example 498.851.15 Example 599.120.88 Example 699.610.39 Example 798.831.17 Example 898.831.17 Example 998,830.590.58 Comparative Example 1100

Table 2

note: in Table 2 octanol is 1-octanol, percent octanol in the raw material list represents the weight percentage concentration in octanol raw material is mixture of octanol and water in the octylene is 1-octene.
C6~C10 alcohol dehydration catalyst for preparing corresponding carbon numbers of olefins *(Translation from Clarivate Analytics)*

Citations

Citation *Record level*

Citing Patents (0)

Cited Patents (2)

	Publication number	Publication date	Application date	Inventor	Assignee/Applicant	Title	Relevance	Source
	US20070043182A1	2007-02-22	2005-11-02	Martin Joel L.		Multimodal polyethylene compositions and pipe made from same	A	0 (Examiner)
	CN102190543A	2011-09-21	2010-03-03	YANG Wei-min	CHINA PETROLEUM & CHEMICAL	Method for preparing ethylene by dehydrating ethanol	YX	0 (Examiner)

Cited Non-patents (2)

- Behrooz Fallah and the like. A New Nano - (2Li2O/MgO) Catalyst/porous α-Alumina Composite for the Oxidative m/z Methane Reaction. "AIChE Journal". 2009, volume 56 (3), page 717-728.

* Behrooz Fallah等.A New Nano-(2Li2O/MgO) Catalyst/Porous Alpha-Alumina Composite for the Oxidative Coupling of Methane Reaction.《AIChE Journal》.2009,第56卷(第3期),第717-728页.

DPCI Citation *Patent family level*

DPCI Citing Patents (0)

DPCI Cited Patents (0)

DPCI Cited Non-patents (0)

DPCI Citation Counts

DPCI Field of search

DPCI Citing Patents Country/Region

DPCI Cited Patents Country/Region

Other

Examiner

Related applications

Parent/Child	Application number	Filed Date	Publication number	Publication date	Type of Relationship	Status
P	CN201410353875A	2014-07-24	CN105312044A	2016-02-10	Related publication	-

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PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To: Lynda L. Calderone
Calderone Bullock LLC
One Greentree Centre
9000 Lincoln Drive East, Suite 301
Marlton, New Jersey 08053
United States of America

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference I0113-198WO	Date of mailing *(day/month/year)* 19 APR 2019 **FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US19/15928	International filing date *(day/month/year)* 30 January 2019 (30.01.2019)
Applicant INOLEX INVESTMENT CORPORATION	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

   When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

   How? Directly to the International Bureau of WIPO preferably through ePCT or on paper to, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Facsimile No.: +41 22 338 82 70

   For more detailed instructions, see *PCT Applicant's Guide*, International Phase, paragraphs 9.004 – 9.011.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to any protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
   ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with any request to forward the texts of both the protest and the decision thereon to the designated Offices.
   ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

   The applicant may **submit comments on an informal basis on the written opinion of the International Searching Authority** to the International Bureau. These comments will be made available to the public after international publication. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established.

   Shortly after the expiration of **18 months from the priority date, the international application will be published** by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau before the completion of the technical preparations for international publication (Rules 90*bis*.1 and 90*bis*.3).

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for **entry into the national phase** before those designated Offices. In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months. For details about the applicable time limits, Office by Office, see www.wipo.int/pct/en/texts/time_limits.html and the *PCT Applicant's Guide*, National Chapters.

   Within **22 months from the priority date, the applicant may request that a supplementary international search be carried out** by a different International Searching Authority that offers this service (Rule 45*bis*.1). The procedure for requesting supplementary international search is described in the *PCT Applicant's Guide*, International Phase, paragraphs 8.006-8.032.

Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas Telephone No. PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/220 (July 2017)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference I0113-198WO	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US19/15928	International filing date *(day/month/year)* 30 January 2019 (30.01.2019)	(Earliest) Priority Date *(day/month/year)* 30 January 2018 (30.01.2018)
Applicant INOLEX INVESTMENT CORPORATION		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 9 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed.

☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (see Box No. II).

3. ☐ **Unity of invention is lacking** (see Box No. III).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

b. ☐ none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US19/15928

A. CLASSIFICATION OF SUBJECT MATTER

IPC - A61K 8/34; A01N 31/00, 31/02; C07C 5/00, 11/10, 11/107; C10G 3/00; B01J 21/00 (2019.01)
CPC - B01J 21/00, 21/005, 21/02, 21/04, 23/00, 23/005, 23/06; C07C 5/00, 11/10, 11/107; C10G 3/00, 3/42, 3/44, 3/45; A61K 8/34, 8/345; A01N 31/00, 31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- A	WO 2016/007196 A1 (COBALT TECHNOLOGIES, INC.) 14 January 2016; paragraphs [22]-[23], [33]-[34], [51], [54], [90], [0103], [122]; claims 1, 29-30, 48; figures 11, 13	35-41 --- 1, 30, 42, 56, 65, 72, 81
A	US 2006/0161025 A1 (OSTERHOLT, C et al.) 20 July 2006; paragraphs [0085]-[0096]	1, 30, 42, 56, 65, 72, 81
A	US 2016/0090331 A1 (IFP ENERGIES NOUVELLES) 31 March 2016; paragraphs [0025]-[0029], [0132]-[0136]; claim 1	1, 30, 42, 56, 65, 72, 81
A	DAI, L et al. Directing enzyme devolution for biosynthesis of alkanols and 1, n-alkanediols from natural polyhydroxy compounds. Metabolic engineering. 1 November 2017. Vol. 44; page 77, figure 7a	1, 30, 42, 56, 65, 72, 81

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 March 2019 (18.03.2019)	19 APR 2019
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: Lynda L. Calderone
Calderone Bullock LLC
One Greentree Centre
9000 Lincoln Drive East, Suite 301
Marlton, New Jersey 08053
United States of America

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)* 19 APR 2019

Applicant's or agent's file reference
I0113-198WO

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US19/15928	30 January 2019 (30.01.2019)	30 January 2018 (30.01.2018)

International Patent Classification (IPC) or both national classification and IPC
IPC - A61K 8/34; A01N 31/00, 31/02; C07C 5/00, 11/10, 11/107; C10G 3/00; B01J 21/00 (2019.01)
CPC - B01J 21/00, 21/005, 21/02, 21/04, 23/00, 23/005, 23/06; C07C 5/00, 11/10, 11/107; C10G 3/00, 3/42, 3/44, 3/45; A61K 8/34, 8/345; A01N 31/00, 31/02

Applicant INOLEX INVESTMENT CORPORATION

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	18 March 2019 (18.03.2019)	Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/237 (cover sheet) (January 2015)

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US18/15928

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a)).

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed:

      ☐ in the form of an Annex C/ST.25 text file.

      ☐ on paper or in the form of an image file.

   b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

   c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

      ☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

      ☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US19/15928

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1-34, 42-87	YES
	Claims	35-41	NO
Inventive step (IS)	Claims	1-34, 42-87	YES
	Claims	35-41	NO
Industrial applicability (IA)	Claims	1-87	YES
	Claims	NONE	NO

2. Citations and explanations:

Claims 35-41 lack novelty under PCT Article 33(2) as being anticipated by WO 2016/007196 A1 to COBALT TECHNOLOGIES, INC. (hereinafter 'Cobalt').

Regarding claim 35, Cobalt discloses a method for treating a catalyst for use in dehydration of alcohols (a method for dehydrating an alcohol to a diene using a catalyst; paragraph [40]; claim 1), comprising providing a gamma-alumina catalyst; treating the gamma-alumina catalyst with a base comprising a Group I or a Group II metal (providing gamma-alumina catalyst treated with Group 1 or Group 2 metal promoters (base); paragraphs [33]-[34], [122]; claims 1, 29); and heating the gamma-alumina catalyst to a temperature of about 400 degree C to about 500 degree C (calcining the treated gamma-alumina catalyst at 100-900 degrees C; paragraphs [33]-[34], [122]).

Regarding claim 36, Cobalt discloses the method according to claim 35, and further discloses wherein the base comprises calcium (treating gamma-alumina catalyst with calcium metal promoters (base); paragraphs [33]-[34], [122]; claim 30).

Regarding claim 37, Cobalt discloses the method according to claim 36, and further discloses wherein the base is a calcium promoter and the heating occurs during calcination (treating gamma-alumina catalyst with calcium metal promoter (base) followed by calcination; paragraphs [33]-[34], [122]).

Regarding claim 38, Cobalt discloses the method according to claim 37, and further discloses wherein the calcium promoter includes is used in an amount of about 0.01 weight percent to about 4 weight percent based on the weight of CaO determined after calcination (Ca-modified catalyst comprising 0.8-4.0 wt. % of Ca+2 deposited on the catalyst support due to calcination (consistent with 1.1-5.6 weight percent based on the weight of CaO, provided the molar mass of Ca is 40g/mol and CaO is 56 g/mol); paragraph [122]).

Regarding claim 39, Cobalt discloses the method according to claim 38, and further discloses wherein the calcium promoter is used in an amount of about 1 weight percent to about 2 weight percent based on the weight of CaO determined after calcination (Ca-modified catalyst comprising 0.8-4.0 wt. % of Ca+2 deposited on the catalyst support due to calcination (consistent with 1.1-5.6 weight percent based on the weight of CaO, provided the molar mass of Ca is 40g/mol and CaO is 56 g/mol); paragraph [122]).

Regarding claim 40, Cobalt discloses the method according to claim 35, and further discloses wherein the temperature during calcination is about 420 degree C to about 480 degree C (calcining the treated gamma-alumina catalyst at 100-900 degrees C; paragraph [122]).

Regarding claim 41, Cobalt discloses the method according to claim 40, and further discloses wherein the temperature during calcination is about 440 degree C to about 460 degree C (calcining the treated gamma-alumina catalyst at 100-900 degrees C; paragraph [122]).

Claim 1 meets the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest the claimed matter.

Regarding claim 1, US 2006/0161025 A1 to OSTERHOLT, et al. (hereinafter 'Osterholt') discloses a process for the synthesis of 1,2-alkanediols (a process for synthesis of 1,2-hexanediol or 1,2-octanediol; paragraphs [0085]-[0096]), comprising: providing an alkene having a carbon chain of about 5 to about 20 carbon atoms; and converting the alkene to a 1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms (providing 1-hexene and converting it into 1,2-hexanediol, or providing 1-octene and converting it to 1,2-octanediol; paragraphs [0085]-[0096]).

Where Osterholt discloses chemical synthesis of 1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms by conversion of alkene (Osterholt, paragraphs [0085]-[0096]), Osterholt fails to disclose a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms synthesized by conversion of a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

-***-Continued Within the Next Supplemental Box-***-

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US19/15928

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

Claim 40 is objected to under PCT Rule 66.2(a)(iii) as containing the following defect in the form or contents thereof: in the line 1 of claim 40, the phrase "The process according to claim 35, temperature", as best understood, is interpreted as "The process according to claim 35, wherein the temperature" for the purpose of this opinion.

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US19/15928

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 39-41 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because claims 39-41 are indefinite for the following reason(s): Claims 39-41 refer to "the process according to claim", in line 1. There is a lack of antecedent basis for these limitations in the claim. For the purpose of this opinion, as best understood, the claims are interpreted to read "the method according to claim".

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:

-***-Continued from Box V: Citations and Explanations-***-

Cobalt discloses a process for the synthesis of bio-alkenes (a process of biomass conversion to bio-dienes (bio-alkenes); figure 1; paragraph [94]), comprising: synthesizing a bio-alkene having a carbon chain of about 4 carbon atoms and a bio-alkene regioselectivity of at least about 80% (dehydration of bio-alcohol to bio-1,3-butadiene with 90-99% regioselectivity; paragraphs [54], [90], [103]); and converting a bio-alcohol to a bio-1,3-alkene having a carbon chain of about 4 carbon atoms (dehydration of bio-alcohol to bio-1,3-butadiene; figure 13; paragraphs [22]-[23]). Cobalt also discloses synthesizing a bio-alkene having a carbon chain of about 4 carbon atoms and a bio-1-alkene yield of at least about 80% (synthesis of 1-butene using catalyst having 80% yield; figure 11; paragraph [51]).

Where Cobalt teaches a process for production of bio-alkenes with high regioselectivity (Cobalt; paragraphs [54], [90], [103]), the process of Cobalt is drawn to the synthesis of bio-alkenes from bio-diols, rather than synthesis of bio-1,2-alkanediols from bio-alkenes. Moreover, the bio-alkene of Cobalt has a shorter chain of only 4 carbon atoms (Cobalt; figures 11, 13; paragraphs [51], [54]).

US 2016/0090331 A1 to IFP ENERGIES NOUVELLES (hereinafter 'Energies') discloses a process for the synthesis of bio-alkanediols, comprising: providing a bio-carbohydrate having a carbon chain of about 5 to about 20 carbon atoms (a process for converting biomass comprising $(C_6H_{10}O_5)_n$ carbohydrates to alkanediols (bio-alkanediols), such as pentanediols and hexanediols, from a long list of compounds; paragraphs [0025]-[0029], [0132]-[0138]; claim 1); and converting the bio-carbohydrate to a bio-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms (converting biomass to alkanediols (bio-alkanediols), such as pentanediols and hexanediols, from a long list of compounds; paragraphs [0025]-[0029], [0132]-[0138]; claim 1).

Where Energies discloses synthesis of bio-alkanediols having a carbon chain of about 5 to about 20 from a bio-carbohydrate (Energies; paragraphs [0025]-[0029], [0132]-[0138]; claim 1), Energies fails to disclose a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms synthesized by conversion of a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

The document entitled 'Directing enzyme devolution for biosynthesis of alkanols and 1,n-alkanediols from natural polyhydroxy compounds' to DAI, et al. (hereinafter 'Dai') discloses a process for the synthesis of bio-1,2-alkanediols (synthesis of 1,2-pentanediol from biomass (bio-1,2-alkanediol); page 77, figure 7A, steps 1-3), comprising: providing a bio-polyhydroxy compounds having a carbon chain of about 5 to about 20 carbon atoms; and converting the bio-polyhydroxy compounds to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms (converting polyhydroxy compounds derived from biomass to 1,2-pentanediol (bio-1,2-alkanediol); page 77, figure 7 A, step 1-3).

Where Dai discloses a process for the synthesis of bio-1,2-alkanediols, comprising: providing a bio-polyhydroxy compounds having a carbon chain of about 5 to about 20 carbon atoms; and converting the bio-polyhydroxy compounds to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms, Dai fails to teach a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms synthesized by conversion of a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

Therefore, the modification of providing for a process for the synthesis of bio-1,2-alkanediols, comprising: providing a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%; and converting the bio-alkene to a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms would not have been obvious to one of ordinary skill in the art at the time of the invention, provided the previous disclosures of Osterholt, Cobalt, Energies, and Dai, as none of the disclosures, taken alone or in combination, teach a 1,2-alkanediols with a carbon atom chain larger than 4, and obtained from a naturally-derived alkene having high bio-1-alkene regioselectivity.

Claims 30, 42, 56, 65, 72, and 81 also meet the criteria set out in PCT Article 33(2)-(3), because claims 30, 42, 56, 65, 72, and 81 share the core inventive element of claim 1, namely, a bio-1,2-alkanediol having a carbon chain length of about 5 to about 20 carbon atoms synthesized by conversion of a bio-alkene having a carbon chain of about 5 to about 20 carbon atoms and a bio-1-alkene regioselectivity of at least about 80%.

Claims 2-29, 31-34, 43-55, 57-64, 66-71, 73-80, and 82-87 also meet the criteria set out in PCT Article 33(2)-(3), because they depend upon claims 30, 42, 56, 65, 72, and 81, respectively.

Claims 1-87 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

Electronic Patent Application Fee Transmittal

Application Number:	16262898
Filing Date:	30-Jan-2019
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	lynda Leigh Calderone/Sandra Calderone
Attorney Docket Number:	I0113-198U1

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
RCE- 1ST REQUEST	1801	1	1300	1300
		Total in USD ($)		**1300**

Electronic Acknowledgement Receipt

EFS ID:	39333685
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	159443
Filer:	lynda Leigh Calderone
Filer Authorized By:	
Attorney Docket Number:	I0113-198U1
Receipt Date:	01-MAY-2020
Filing Date:	30-JAN-2019
Time Stamp:	22:24:17
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1300
RAM confirmation Number	E202051M25198773
Deposit Account	602689
Authorized User	Lynda Calderone

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Request for Continued Examination (RCE)	RCERequest.pdf	121258 3981114c88a84c020c518476996e81212dcf21db	no	2
Warnings:					
This is not a USPTO supplied RCE SB30 form.					
Information:					
2	Transmittal Letter	IDS.pdf	112577 2ac1541cb1048613914b1f38495ec447640ed4e8	no	2
Warnings:					
Information:					
3	Information Disclosure Statement (IDS) Form (SB08)	PTOSB08A.pdf	179185 68a180b9bf37d4f00bb9bc83f025f0bafe1fcbaf	no	1
Warnings:					
Information:					
This is not an USPTO supplied IDS fillable form					
4	Foreign Reference	WO2004078336A2.pdf	1775727 98d817d3d1bef31c8f19be1fb0daf82a1ce15eb1	no	13
Warnings:					
Information:					
5	Foreign Reference	WO2013077904A1.pdf	1583884 6a325cdfa598012e299711cc89a26b692ca7ed11	no	19
Warnings:					
Information:					
6	Foreign Reference	WO2013106065A1.pdf	3570847 f83c65da3b4f4eac1f65f231b730346dea2be434	no	26

Warnings:					
Information:					
7	Foreign Reference	CN105312044.pdf	4946890 6dbe76cbc18a33af611f7e796d7c53ce55de6f94	no	21
Warnings:					
Information:					
8	Non Patent Literature	MetabolicEngineering.pdf	1060002 69b4b008f2ddc3433c6ce5d91940e42eb800b7b0	no	11
Warnings:					
Information:					
9	Other Reference-Patent/App/Search documents	ISRWO.pdf	656914 acf13d69933ce09fe532cf912c657c885bcb8d22	no	9
Warnings:					
Information:					
10	Non Patent Literature	D686605.PDF	389294 0a42546eacaa219faceb9fe9fdbb4778e30d443f	no	14
Warnings:					
Information:					
11	Fee Worksheet (SB06)	fee-info.pdf	30431 89e60c021c77ffec4f1982a370299b7c5e6e7c2f	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	14427009	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

159443 7590 05/21/2020

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

EXAMINER
CUTLIFF, YATE KAI RENE

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 05/21/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	08/21/2020

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

159443 7590 05/21/2020

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	08/21/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑ Issue Fee ❑ Publication Fee (if required) ❑ Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1	3410

159443 7590 05/21/2020

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

EXAMINER	
CUTLIFF, YATE KAI RENE	
ART UNIT	**PAPER NUMBER**
1622	

DATE MAILED: 05/21/2020

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/262,898	Applicant(s) Burgo et al.	
	Examiner YATE K CUTLIFF	Art Unit 1622	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to RCE of 5/1/2020.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-34 and 88-91 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 5/1/2020.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Continued Examination Under 37 CFR 1.114

2. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after allowance or after an Office action under *Ex Parte Quayle*, 25 USPQ 74, 453 O.G. 213 (Comm'r Pat. 1935). Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, prosecution in this application has been reopened pursuant to 37 CFR 1.114. Applicant's submission filed on May 1, 2020 has been entered.

Information Disclosure Statement

3. The information disclosure statement (IDS) submitted on May 1, 2020 was filed after the mailing date of the Notice of Allowance on April 13, 2020. The submission is in compliance with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

4. The information disclosure statement (IDS) submitted on May 1, 2020 listed the incorrect U. S. Patent Document Number 8,345,007, for Wright et al. (#5). The correct U. S. Patent Document Number is 8,395,007, published March 2013. The Examiner corrected the IDS to reflect the correct U. S. Patent Document Number.

Allowable Subject Matter

5. Claims 1 – 34 and 88 – 91 are allowed.

6. The following is an examiner's statement of reasons for allowance: claims are allowed for the reasons set out in the Notice of Allowance mailed April 13, 2020 and reasons of record.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to YATE K. CUTLIFF whose telephone number is (571)272-9067. The examiner can normally be reached on Monday-Friday (8:30 - 5:30).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf can be reached on (571) 272 - 2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR.

Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC - Searched*		
Symbol	Date	Examiner
C07C 29/04, 48	04/03/2020	ykc
C07C 31/20	04/03/2020	ykc
C07C 33/025	08/01/2019	ykc
C07C 2521/04	04/03/2020	ykc
B01J 21/04	04/03/2020	ykc
B01J 23/06	08/01/2019	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	04/03/2020	ykc
C07B 41/02	04/03/2020	ykc

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

Search Notes		
Search Notes	**Date**	**Examiner**
Palm Inventor Search	05/18/2020	ykc
East	05/18/2020	ykc
C07C 29/04, 48	05/18/2020	ykc
C07C 31/20	05/18/2020	ykc
C07C 33/025	08/01/2019	ykc
C07C 2521/04	05/18/2020	ykc
B01J 21/04	05/18/2020	ykc
B01J 23/06	08/01/2019	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	05/18/2020	ykc
C07B 41/02	05/18/2020	ykc

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
C07C	29/04, 48	05/18/2020	ykc
C07C	31/20	05/18/2020	ykc
C07C	2521/04	05/18/2020	ykc
B01J	21/04	05/18/2020	ykc
C07C	11/02, 107	05/18/2020	ykc
C07B	41/02	04/03/2020	ykc

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC								
Symbol							Type	Version
C07C	/	29	/	04			F	2013-01-01
C07C	/	31	/	20			I	2013-01-01
C07C	/	29	/	80			I	2013-01-01
B01J	/	23	/	06			I	2013-01-01
B01J	/	37	/	08			I	2013-01-01
B01J	/	21	/	04			I	2013-01-01
C11D	/	3	/	2044			I	2013-01-01
C11D	/	3	/	48			I	2013-01-01
C07C	/	1	/	24			I	2013-01-01
C07C	/	29	/	48			I	2013-01-01
C07C	/	11	/	02			I	2013-01-01
C07C	/	11	/	107			I	2013-01-01
B01J	/	2523	/	27			A	2013-01-01
C07B	/	41	/	02			A	2013-01-01
C07B	/	63	/	00			A	2013-01-01
B01J	/	2523	/	31			A	2013-01-01
A61L	/	2	/	18			A	2013-01-01
A01N	/	31	/	02			A	2013-01-01
A61K	/	8	/	345			A	2013-01-01
A61Q	/	5	/	00			A	2013-01-01
A61Q	/	11	/	00			A	2013-01-01
A61Q	/	19	/	00			A	2013-01-01
C07C	/	2521	/	04			A	2013-01-01

CPC Combination Sets									
Symbol							Type	Set	Ranking	Version
C07C	/	1	/	24			I	1	1	2013-01-01
C07C	/	11	/	02			I	1	2	2013-01-01
C07C	/	29	/	48			I	2	1	2013-01-01
C07C	/	31	/	20			I	2	2	2013-01-01

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	18 May 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20200518

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CPC Combination Sets												
Symbol							**Type**	**Set**	**Ranking**	**Version**		
C07C	/	29	/	80			I	3	1	2013-01-01		
C07C	/	31	/	20			I	3	2	2013-01-01		

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	18 May 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

INTERNATIONAL CLASSIFICATION					
CLAIMED					
C07C	/	29	/	04	
C07C	/	29	/	48	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE (Assistant Examiner) (Date)	**Total Claims Allowed:** 38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622 (Primary Examiner) 18 May 2020 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	13	13	25	25		37		49		61		73		85
2	2	14	14	26	26		38		50		62		74		86
3	3	15	15	27	27		39		51		63		75		87
4	4	16	16	28	28		40		52		64		76	35	88
5	5	17	17	29	29		41		53		65		77	36	89
6	6	18	18	30	30		42		54		66		78	37	90
7	7	19	19	31	31		43		55		67		79	38	91
8	8	20	20	32	32		44		56		68		80		
9	9	21	21	33	33		45		57		69		81		
10	10	22	22	34	34		46		58		70		82		
11	11	23	23		35		47		59		71		83		
12	12	24	24		36		48		60		72		84		

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622 (Primary Examiner)	18 May 2020 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure 1

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020	05/18/2020						
	1	✓	=	=						
	2	✓	=	=						
	3	✓	=	=						
	4	✓	=	=						
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	38	✓	-	-						
	39	✓	-	-						
	40	✓	-	-						
	41	✓	-	-						
	42		-	-						

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020	05/18/2020						
	43		-	-						
	44		-	-						
	45		-	-						
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	88		=	=						
	89		=	=						
	90		=	=						
	91		=	=						

Form PTO/SB/08A				Complete if Known	
INFORMATION DISCLOSURE STATEMENT BY APPLICANT				**Application Number**	16/262,898
				Filing Date	January 30, 2019
				First Named Inventor	Rocco V. Burgo
(use as many sheets as necessary)				**Group Art Unit**	1622
				Examiner Name	Yate Kai Rene Cutliff
Sheet	1	of	1	**Attorney Docket Number**	I0113-198U1

U.S. PATENT DOCUMENTS				
Exr Initials	U.S. Patent Document Number	Kind Code (if known)	Name of First Inventor of Cited Document	Date of Publication of Cited Document MM-YYYY
	2005/0069997	A1	Adkesson	03-2005
	2006/0161025	A1	Osterholt	07-2006
	2007/0207105	A1	Winn	09-2007
	7,576,250	B2	Gao	08-2009
8395007	8,345,007	B2	Wright	03-2013
	9,029,619	B2	Vermeiren	05-2015
	9,242,226	B2	Wright	01-2016
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	2017/0360035	A1	Winn	12-2017

FOREIGN PATENT DOCUMENTS						
Exr Initials	Foreign Patent Document Country Code	Number	Kind Code (if known)	Name of Applicant of Cited Document	Date of Publication of Cited Document MM-YYYY	T_1
	WO	2004/078336	A2	Ziehe	09-2004	
	WO	2013/077904	A1	Wright	05-2013	
	WO	2013/106065	A1	Wright	07-2013	
	CN	105312044	B1	Jin	02-2018	

OTHER PRIOR ART - NON PATENT LITERATURE DOCUMENTS		
Exr Initials	Include Name of first Author (in CAPITAL LETTERS), title of the article (where appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), volume-issue number(s), page(s), date (in parentheses). If a book, also include publisher and city and/or county where published.	T_1
	DAI LU, Directing enzyme devolution for biosynthesis of alkanols and 1,n-alkanediols from natural polyhydroxy compounds, Metabolic Engineering. 1 Nov 2017, Vol. 44, p. 77, Fig 7a	
	International Search Report and Written Opinion of International Application No. PCT/US19/15928 dated April 19, 2019	
	ASTMD6866-05, Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotape Ratio Mass Spectrometry Analysis, March 1, 2005	

Examiner Signature	/YATE' K CUTLIFF/	Date Considered	05/18/2020

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /Y.K.C/

T_1 - Place a check mark if complete translation document is in English; otherwise, place a letter "A" if only an English abstract is attached.

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CONFIRMATION NO. 3410

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
16/262,898	01/30/2019	568	1622	I0113-198U1

APPLICANTS

Inolex Investment Corporation, Wilmington, DE

INVENTORS

Rocco V. Burgo, Mullica Hill, NJ;
Michael E. Wright, Hurricane, UT;
Gary B. Mosser, Tabernacle, NJ;
Michael J. Fevola, Belle Mead, NJ;

**** CONTINUING DATA ***************************

This appln claims benefit of 62/623,985 01/30/2018

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

02/15/2019

Foreign Priority claimed ☐ Yes ☑ No 35 USC 119(a-d) conditions met ☐ Yes ☑ No Verified and Acknowledged /YATE KAI RENE CUTLIFF/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		NJ	7	41	3

ADDRESS

Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053
UNITED STATES

TITLE

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

FILING FEE RECEIVED		
3980	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:57
S2	69	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S3	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S4	69	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S5	2	"2016007196".pn.	US-PGPUB; USPAT; USOCR; FPRS; EPO	OR	OFF	2019/07/31 11:33
S6	9189	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:43
S7	1392	(natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:45
S8	23	S6 and S7 and alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 12:46
S9	9170	(method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50

S10	684	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and dehydration	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S11	378	S10 and (natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:51
S12	125	S11 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:02
S13	125	S12 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:03
S14	9170	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S15	1219	S14 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:05
S16	1175	S15 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S17	55	S14 and (terminal with (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:07
S18	3	("20050006997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:29
S19	3	("20050069997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:30

S20	5912	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:35
S21	2221	S20 and (natural or plant or vegetable or ferment$4 or biomass)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:40
S22	312	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and (peracid or formic of acetic) and (hydrogen adj peroxide)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S23	308	S22 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S24	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:51
S25	3031	C07C29/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:15
S26	5809	C07C31/20.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S27	0	C07C33/25.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S28	3127	C07C33/025.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	OFF	2019/07/31 14:17

			DERWENT; IBM_TDB			
S29	18997	B01J21/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S30	16230	B01J37/08.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:18
S31	4501	B01J23/06.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:21
S32	14742	c07c2521/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:22
S33	38	S25 and S28	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:23
S34	2	S20 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:24
S35	5	S28 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:25
S36	0	S25 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	OFF	2019/07/31 14:26

			DERWENT; IBM_TDB			
S37	0	S33 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S38	1	"7385092".pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 16:49
S39	1	"20170360035".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/08/01 10:10
S40	13	(biodiene? or (bio adj diene?) or (bio adj alkene) or bioalkene)	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/08/01 10:27
S41	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:13
S42	27	S41 and hydrolysis	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:13
S43	9195	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:16
S44	886	S43 and hydrolysis	USPAT	OR	OFF	2019/08/01 11:16
S45	24	S43 and hydrolysis and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:17

S46	5	S43 and (hydroxide with hydrolysis) and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:24
S47	1	"20140066666".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:26
S48	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:29
S49	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:30
S50	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S51	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S52	2015	c07c29/48.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:49
S53	1075	c07b41/02.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:54
S54	24629	c07c11/02,107.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S55	32	S53 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S56	9	S55 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	OFF	2020/04/03 12:55

			DERWENT; IBM_TDB			
S57	23	S52 and S53	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S58	5	S57 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S59	48	S52 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:58
S60	6	S59 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:58
S77	13	("20050006997," "20060161025," "20160090331," "20170360035," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 11:20
S78	14	("20050006997," "20060161025," "20160090331," "20170360035," "7385092," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 11:31
S79	3	S78 and (alkanediol or octanediol)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 11:49
S80	3	S78 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO;	OR	OFF	2020/05/18 11:50

			DERWENT; IBM_TDB			
S81	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/05/18 12:03
S82	14	("20050069997," "20060161025," "20160090331," "20170360035," "7385092," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 12:18
S83	15	("20050069997," "20060161025," "20070207105," "20160090331," "20170360035," "7385092," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 12:22
S84	5	S83 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 12:23
S85	8	("2004078336," "2013077904," "2013106065," "105312044").pn.	FPRS; EPO	OR	OFF	2020/05/18 12:25
S86	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:28
S87	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S88	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S89	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35

EAST Search History (Interference)

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S61	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/04/03 13:00

S62	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S63	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S64	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S65	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S66	698	C07C31/20.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S67	251	c07c29/48.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S68	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S69	3196	c07c11/02,107.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S70	2105	B01J21/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S71	2140	c07c2521/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S72	2	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S69	USPAT	OR	OFF	2020/04/03 13:07
S73	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S66	USPAT	OR	OFF	2020/04/03 13:09
S74	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S65	USPAT	OR	OFF	2020/04/03 13:10
S75	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S67	USPAT	OR	OFF	2020/04/03 13:10
S76	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S68	USPAT	OR	OFF	2020/04/03 13:10
S90	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/05/18 12:40

S91	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/05/18 12:40
S92	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/05/18 12:40
S93	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/05/18 12:41
S94	3211	c07c11/02,107.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S95	2128	B01J21/04.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S96	2151	c07c2521/04.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S97	2	(S90 or S91 or S92) and S94 and (S95 or S96) and S94	USPAT	OR	OFF	2020/05/18 12:41
S98	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/05/18 12:43
S99	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S98	USPAT	OR	OFF	2020/05/18 12:43
S100	2	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S94	USPAT	OR	OFF	2020/05/18 12:43
S101	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S98	USPAT	OR	OFF	2020/05/18 12:44
S102	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/05/18 12:44
S103	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S102	USPAT	OR	OFF	2020/05/18 12:44

5/18/2020 12:47:31 PM
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Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
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Application Number	16/262,898
Filing Date	January 30, 2019
First Named Inventor	Rocco Burgo
Title	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
Art Unit	1622
Examiner Name	CUTLIFF, YATE KAI RENE
Attorney Docket Number	I0113-198U1

SIGNATURE of Applicant or Patent Practitioner

Signature	/Eric J. Choi/	Date (Optional)	
Name	Eric J. Choi	Registration Number	71,160
Title (if Applicant is a juristic entity)	Attorney		
Applicant Name (if Applicant is a juristic entity)	Inolex Investment Corporation		

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ *Total of 1 forms are submitted.

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POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 171052

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number:

OR

☐ Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

INOLEX Investment Corporation

☐ Inventor or Joint Inventor (title not required below)
☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)
☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)
☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature	/David C.A. Plimpton/	Date (Optional)	5.22.2020
Name	David C.A. Plimpton		
Title	CEO & President		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☐ Total of forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/82C (07-13)
Approved for use through 03/31/2021. OMB 0651-0035
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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POWER OF ATTORNEY BY APPLICANT

No more than ten (10) patent practitioners total may be appointed as set forth below by name and registration number. This page need not be submitted if appointing the Patent Practitioner(s) associated with a Customer Number (see form PTO/AIA/82B):

Name	Registration Number

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	40175323
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	159443
Filer:	Eric J. Choi/Valerie Dotson
Filer Authorized By:	Eric J. Choi
Attorney Docket Number:	I0113-198U1
Receipt Date:	03-AUG-2020
Filing Date:	30-JAN-2019
Time Stamp:	13:34:18
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Power of Attorney	INLX_198U1_484809_IO113-198U1_PowerOfAttorney.pdf	333982 79a85b9d4089d4f011a2a7eab907bec698ba8702	no	4

Warnings:

Information:	
Total Files Size (in bytes):	333982

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1

CONFIRMATION NO. 3410

171052
Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

POA ACCEPTANCE LETTER

OC000000118955814

Date Mailed: 08/05/2020

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 08/03/2020.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/yteferra/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/262,898	01/30/2019	Rocco V. Burgo	I0113-198U1

CONFIRMATION NO. 3410

POWER OF ATTORNEY NOTICE

159443
Calderone Bullock LLC
Two Greentree Centre, Suite 301
9000 Lincoln Drive East
Marlton, NJ 08053

OC00000018955774

Date Mailed: 08/05/2020

NOTICE REGARDING CHANGE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 08/03/2020.

- The Power of Attorney to you in this application has been revoked by the applicant. Future correspondence will be mailed to the new address of record(37 CFR 1.33).

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/yteferra/

PTO/SB/30EFS (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
(Submitted Only via EFS-Web)

Application Number	16262898	Filing Date	2019-01-30	Docket Number (if applicable)	INLX.0198U1/484809	Art Unit	1622
First Named Inventor	Rocco V. Burgo			Examiner Name	CUTLIFF, YATE KAI RENE		

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

- ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____
- ☐ Other _____

☒ Enclosed

- ☐ Amendment/Reply
- ☒ Information Disclosure Statement (IDS)
- ☐ Affidavit(s)/ Declaration(s)
- ☐ Other _____

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____ (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

☒ **The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.**
The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 503111

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

Applicant Signature

PTO/SB/30EFS (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Signature of Registered U.S. Patent Practitioner			
Signature	/Eric J. Choi/	Date (YYYY-MM-DD)	2020-08-21
Name	Eric J. Choi	Registration Number	71160

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Attorney Docket # INLX.0198U1/484809

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of INOLEX INVESTMENT CORPORATION Serial No.: 16/262,898 Filed: January 20, 2019 For: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same	Examiner: CUTLIFF, YATE KAI RENE. Group Art: 1622

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

INFORMATION DISCLOSURE STATEMENT

S I R:

In compliance with the duty of disclosure under 37 C.F.R. §1.56 and in accordance with the practice under 37 C.F.R. §§1.97 and 1.98, the Examiner's attention is directed to the documents listed on the enclosed Form PTO/SB/08a. Copies of the listed non-US documents and non-patent literature are also enclosed.

This information is being submitted after issuance of the Notice of Allowance, and after payment of the Issue Fee.

STATEMENT

No item of information contained in the Information Disclosure Statement was cited in a communication from a foreign Patent Office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, each item of information contained in the Information Disclosure Statement was first cited in a third party submission filed in the patent application counterpart, U.S. Patent Application No.16/262,902.

In accordance with 37 C.F.R §§1.97(g) and (h), the filing of this Information Disclosure Statement should not be construed as a representation that a search has been made or that information cited is, or is considered to be, material to patentability as defined in §1.56(b), or that any cited document listed or attached is (or constitutes) prior art. Unless otherwise indicated, the date of publication indicated for an item is taken from the face of the item and Applicant(s) reserve(s) the right to prove that the date of publication is in fact different.

Submitted herewith is the required fee of $240.00 under 37 C.F.R. § 1.17(p), If any other fees or charges are required at this time, they may be charged to our Patent and Trademark Office Deposit Account No. 503111.

It is respectfully requested that the above information be considered by the Examiner and that a copy of the enclosed Form PTO/SB/08a be returned indicating that such information has been considered.

Respectfully submitted,
COZEN O'CONNOR

By /Eric J. Choi/
Eric J. Choi
Reg. No. 71, 160
1200 19th Street NW, 3rd Floor
Washington, DC 20036
(202) 912-4841

Dated: August 21, 2020

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16262898
Filing Date	2019-01-30
First Named Inventor	Rocco V. Burgo
Art Unit	1622
Examiner Name	CUTLIFF, YATE KAI RENE
Attorney Docket Number	INLX.0198U1/484809

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	4234752		1980-11-18	Yulin Wu	
	2	8912373	B2	2014-12-16	Michael Wright	
	3	9856461	B2	2018-01-02	Jeffrey Fortman	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20140066666	A1	2014-03-06	Oskar Koch	
	2	20050065389	A1	2005-03-24	De Bruyn	
	3	20030065233	A1	2003-04-03	Fuji	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

	4	20060161025	A1	2008-06-10	Swern			

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	1876162	EP	A1	2008-01-09	Furuya		

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	Wang et al., Efficient conversion of microcrystalline cellulose to 1,2-alkanediols over supported Ni catalysts, GREEN CHEM., 14:758-765 (2012)	
	2	Jong & Birmingham, Mushrooms as a Source of Natural Flavor and AromaCcompouds", Chapter 37 (pp. 345-366) in MUSHROOM BIOLOGY AND MUSHROOM PRODUCTS (Chinese University Press 1993)	
	3	Swern et al., Hydroxylation and Epoxidation of Some 1-Olefins with Per-acids, JACS, 68:1504-1507 (1946)	
	4	Klug et al., Degradation of Hydrocarbons by Members of the Genus Candida, II. Oxidation of n-Alkanes and 1-Alkenes by Candida lipolytica, Journal of Bacteriology, Vol. 93, No. 6, pp 1847-1852 (1964)	
	5	Liu et al., Hydrogen peroxide-independent production of α-alkenes by OleTJE P450 fatty acid decarboxylase, Biotechnology for Biofuels, 7:28 (2014)	

If you wish to add additional non-patent literature document citation information please click the Add button Add

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

EXAMINER SIGNATURE			
Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Eric J. Choi/	Date (YYYY-MM-DD)	2020-08-21
Name/Print	Eric J. Choi	Registration Number	71,160

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Application Number:	16262898
Filing Date:	30-Jan-2019
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First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	Eric J. Choi/Valerie Dotson
Attorney Docket Number:	INLX.0198U1/484809

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

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Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
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Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
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(54) ALKANEDIOL COMPOSITION, PROCESS FOR PRODUCING THE SAME AND COSMETIC

(57) A less malodorous alkanediol composition, a process for producing the alkanediol composition efficiently, and a cosmetic containing the alkanediol composition are provided.

An alkanediol composition contains 0.005 parts by mass or less of ester compound per 100 parts by mass of alkanediol compound having four or more carbon atoms. An alkanediol composition contains 0.2 parts by mass or less of dioxane compound per 100 parts by mass of alkanediol compound having four or more carbon atoms. Furthermore, an ether-containing dihydric alcohol is preferably 0.3 parts by mass or less per 100 parts by mass of alkanediol compound.

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Description

Technical Field

[0001] The present invention relates to an alkanediol composition, a process for producing the alkanediol composition, and a cosmetic, and more particularly to an alkanediol composition that contains little specific by-products and that generates no unpleasant smell, a process for producing the alkanediol composition, and a cosmetic.

Background Art

[0002] It is unavoidable for manufacturers of organic compounds that organic chemical reactions are associated with the formation of by-products. The amount of by-product is often much smaller than that of end product. However, even a small amount of by-product sometimes chemically affects an end product, for example, by worsening the color or smell of the end product. For manufacturers of organic compounds, preventing the formation of disadvantageous by-products or finally removing disadvantageous by-products to prevent these adverse effects is part of manufacturing processes.

[0003] In such a situation, alkanediol compounds have been used in various applications, such as cosmetic preservatives and humectants, pearling agents, raw materials for synthetic fiber, raw materials for urethane compounds, and water-based inks. However, particularly in cosmetic applications, the smell of alkanediol compounds formulated in products causes a big problem. For example, the addition of an alkanediol compound to a product free from a perfume impairs the unscented product. Even in a product containing a perfume, the addition of a malodorous alkanediol compound changes the smell of the product. Hence, there has been a great demand for an odorless or less malodorous alkanediol composition in cosmetic applications.

[0004] A currently common process for producing an alkanediol composition includes oxidizing an olefin with an oxidizing agent such as hydrogen peroxide to produce an epoxy compound and hydrolyzing the epoxy compound. Because an alkanediol composition thus produced has a smell, the alkanediol composition is usually purified by distillation, which is a common purification method (see Patent Documents 1 and 2, for example).

[0005] Patent Document 1: Japanese Unexamined Patent Application Publication No. 57-62234

[0006] Patent Document 2: Japanese Unexamined Patent Application Publication No. 60-78928

Disclosure of Invention

Problems to be Solved by the Invention

[0007] However, as described in Patent Document 1 or 2, alkanediol compositions have a smell even after distillation. This is because a component causing a smell is not identified, and the distillation is performed without knowing the component to be removed. Accordingly, it is an object of the present invention to provide a less malodorous alkanediol composition, a process for producing the alkanediol composition efficiently, and a cosmetic containing the alkanediol composition.

Means for Solving the Problems

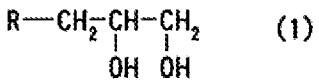
[0008] As a result of diligent investigations on the above-mentioned problems, the present inventors identified a specific component causing a smell in an alkanediol composition and perfected the present invention by discovering that a less malodorous alkanediol composition can be produced by reducing the specific compound to a certain level.

[0009] Thus, an alkanediol composition according to the present invention contains 0.005 parts by mass or less of ester compound (A) per 100 parts by mass of alkanediol compound having four or more carbon atoms.

[0010] Furthermore, another alkanediol composition according to the present invention contains 0.2 parts by mass or less of dioxane compound (C) per 100 parts by mass of alkanediol compound having four or more carbon atoms.

[0011] Furthermore, in the present invention, an ether-containing dihydric alcohol (B) is preferably 0.3 parts by mass or less per 100 parts by mass of alkanediol compound.

[0012] Furthermore, an alkanediol compound having a general formula (1) can suitably be used in the present invention:



$$R\text{—}CH_2\text{—}\underset{\underset{OH}{|}}{CH}\text{—}\underset{\underset{OH}{|}}{CH_2} \qquad (1)$$

wherein R denotes an alkyl group having 4-15 carbon atoms. Furthermore, the alkanediol compound is preferably a hydrolysate of an epoxy compound produced by an oxidation reaction of an olefin.

[0013] Furthermore, a process for producing an alkanediol composition according to the present invention includes the steps of (a) oxidizing an olefin to produce an epoxy compound, (b) hydrolyzing the epoxy compound to produce the alkanediol composition, and (c) adding water and/or an organic solvent to the alkanediol composition and removing water and/or the organic solvent under reduced pressure.

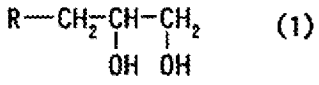
[0014] A cosmetic according to the present invention contains an alkanediol composition according to the present invention. Advantages of the Invention

[0015] An alkanediol composition according to the present invention has little smell. Furthermore, cosmetics containing an alkanediol composition according to the present invention do not have any problem caused by the smell of the alkanediol composition. An alkanediol composition containing a low concentration of component causing a smell can efficiently be produced by a process for producing an alkanediol composition according to the present invention.

Best Mode for Carrying Out the Invention

[0016] An alkanediol compound that can be used in the present invention has at least four carbon atoms. In addition, any two hydrogen atoms of a saturated aliphatic hydrocarbon of the alkanediol compound are replaced by hydroxyl groups. Examples of the alkanediol compound include 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, isoprene glycol (3-methyl-1,3-butanediol), 1,2-hexanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,2-octanediol, 2,3-octanediol, 2-ethyl-1,3-hexanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,5-dimethyl-2,5-hexanediol, 1,2-decanediol, 1,2-dodecanediol, 1,2-tetradecanediol, 1,2-hexadecanediol, 1,2-octadecanediol, 1,12-octadecanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, and 1,4-cyclohexanedimethanol.

[0017] Among others, vicinal compounds that have two hydroxyl groups on adjacent carbon atoms are preferred. Compounds having a general formula (1) are more preferred:



(1)

wherein R denotes an alkyl group having 4-15 carbon atoms. Examples of the alkyl group include a butyl group, an isobutyl group, a secondary butyl group, a tertiary butyl group, a pentyl group, an isopentyl group, a secondary pentyl group, a neopentyl group, a tertiary pentyl group, a hexyl group, a secondary hexyl group, a heptyl group, a secondary heptyl group, an octyl group, a secondary octyl group, a nonyl group, a secondary nonyl group, a decyl group, a secondary decyl group, an undecyl group, a secondary undecyl group, a dodecyl group, a secondary dodecyl group, a tridecyl group, an isotridecyl group, a secondary tridecyl group, a tetradecyl group, a secondary tetradecyl group, a hexadecyl group, a secondary hexadecyl group, a stearyl group, a 2-ethylhexyl group, a 2-butyloctyl group, a 2-butyldecyl group, and a 2-hexyloctyl group.

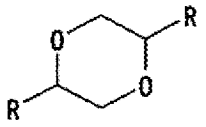
[0018] The alkyl groups preferably have 4-9 carbon atoms, more preferably 4-7 carbon atoms, still more preferably 4-6 carbon atoms, and most preferably 5 carbon atoms.

[0019] While an alkanediol composition according to the present invention may be produced by any process, the alkanediol composition may be produced by oxidizing an olefin into an epoxy compound and subsequently hydrolyzing the epoxy compound. The olefin may be oxidized with an oxidizing agent, such as hydrogen peroxide, a peroxide compound, or an inorganic oxidizing agent. The epoxy compound may be hydrolyzed by a direct reaction with water under high pressure or by a reaction between the epoxy compound and formic acid or acetic acid, followed by hydrolysis with an alkaline substance. Alkanediol compositions thus produced always contain by-products, such as ester compounds, unsaturated alcohols, or acetal compounds. However, compounds causing smells have not been identified. Thus, alkanediol compositions are usually purified by distillation, which is a common purification method, as described above. However, smells of the alkanediol compositions cannot be removed by distillation alone.

[0020] As a result of investigations, the present inventors found that ester compounds and dioxane compounds have the largest influence on the smell among compounds causing smells. In an alkanediol composition according to a first embodiment of the present invention, therefore, the content of an ester compound (A) must be 0.005 parts by mass or less per 100 parts by mass of alkanediol compound. The term "ester compound (A)" means a compound having an ester bond and includes reaction products between epoxy compounds and fatty acids, such as formic acid and acetic acid, reaction products between alkanediol compounds and fatty acids, and reaction products between compounds having a carbonyl group, which are produced by the oxidation of olefins, and epoxy compounds or alkanediol compounds. These

ester compounds cause a smell. Hence, the content of an ester compound in an alkanediol composition according to the present invention is 0.005 parts by mass or less, preferably 0.003 parts by mass or less, and more preferably 0.001 parts by mass or less per 100 parts by mass of alkanediol compound. More than 0.005 parts by mass of ester compound (A) in an alkanediol composition causes an unpleasant smell.

[0021] In an alkanediol composition according to a second embodiment of the present invention, the content of a dioxane compound (C) must be 0.2 parts by mass or less per 100 parts by mass of alkanediol compound. In the present invention, reduction in the amount of dioxane compound (C) can also reduce a smell. Examples of the dioxane compound (C) include compounds having general formulae (2) and (3) (wherein R is as defined above). The dioxane compound (C) may be produced by a dehydration condensation reaction of alkanediols or a condensation reaction of unreacted epoxy compounds. The content of the dioxane compound (C) in an alkanediol composition according to a second embodiment of the present invention is 0.2 parts by mass or less, preferably 0.15 parts by mass or less, and more preferably 0.1 parts by mass or less per 100 parts by mass of alkanediol compound. More than 0.2 parts by mass of dioxane compound (C) in an alkanediol composition causes an unpleasant smell.



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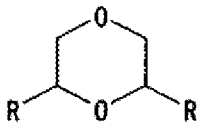
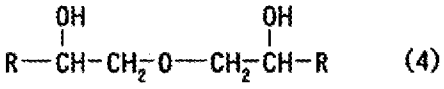


(3)

[0022] In the present invention, as described above, reduction of the content of either the ester compound (A) or the dioxane compound (C) leads to a less malodorous alkanediol composition. Another by-product causing a smell of an alkanediol composition is an ether-containing dihydric alcohol. Examples of the ether-containing dihydric alcohol (B) include compounds having general formulae (4), (5), and (6) (wherein R is as defined above). The ether-containing dihydric alcohol (B) may be produced by a dehydration condensation reaction of alkanediols. The content of the ether-containing dihydric alcohol (B) in an alkanediol composition according to the present invention is preferably 0.3 parts by mass or less, more preferably 0.2 parts by mass or less, and still more preferably 0.15 parts by mass or less per 100 parts by mass of alkanediol compound. More than 0.3 parts by mass of ether-containing dihydric alcohol (B) in an alkanediol composition causes an unpleasant smell.



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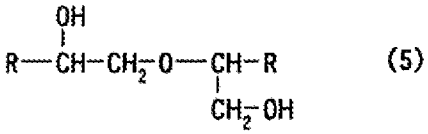

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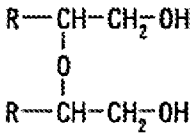


(6)

[0023] Such a by-product may be analyzed by a method using an analyzer, such as gas chromatography, liquid chromatography, a mass spectrometer, NMR, or IR, or by titration analysis of a saponification value, the degree of unsaturation, or a hydroxyl value. In terms of microanalysis of a by-product, the by-product may be analyzed preferably by instrumental analysis, more preferably by gas chromatography or with a mass spectrometer, and still more preferably by gas chromatography. In an alkanediol composition according to the present invention, because the peak area ratio in a gas chromatography chart indicates the mass ratio, the mass ratio of each component can easily be determined.

[0024] Gas chromatography analysis may be performed under any condition under which a by-product can be separated. Exemplary conditions are as follows: a gas chromatograph GC-14B (Shimadzu Corporation) with a J & W Scientific DB-1 column (100% dimethylpolysiloxane, inner diameter 0.53 mm, length 15 m, film thickness 1.5 μm); a 20 ml/min nitrogen carrier gas; an FID detector temperature of 320°C; an air pressure of 50 kPa; a hydrogen pressure of 50 kPa; and a vaporization chamber temperature of 320°C. The column may be held at 60°C for five minutes, be heated to 280°C at 10°C/min, and be held at 280°C for three minutes. 0.1 μl of sample diluted to 1.5% by weight in ethanol may be injected with a microsyringe.

[0025] Under the conditions described above, a main peak of 1,2-octanediol appears at a retention time of about 10 min. A peak of a by-product, if any, appears before or after the main peak. The peak area ratio indicates the mass ratio of each component. A peak of an ester compound appears zero to two minutes before the retention time of the main peak. A peak of a dioxane compound appears four to seven minutes after the retention time of the main peak. A peak of an ether-containing dihydric alcohol appears eight to fifteen minutes after the retention time of the main peak.

[0026] In an alkanediol composition according to a first embodiment of the present invention, the peak area of an ester compound appearing zero to two minutes before the retention time of the main peak must be 0.005% or less, preferably 0.003% or less, and more preferably 0.001% or less of the main peak area. When the peak area of an ester compound exceeds 0.005% of the main peak area, the content of the ester compound exceeds 0.005 parts by mass per 100 parts by mass of alkanediol compound. A component causing a smell and having an unknown structure may appear zero to two minutes after the retention time of the main peak. A peak in this area is therefore indicative of a strong smell and is not preferred.

[0027] In an alkanediol composition according to a second embodiment of the present invention, the peak area of a dioxane compound appearing four to seven minutes after the retention time of the main peak must be 0.2% or less, preferably 0.15% or less, and more preferably 0.1% or less of the main peak area. When the peak area of a dioxane compound exceeds 0.2% of the main peak area, the content of the dioxane compound exceeds 0.2 parts by mass per 100 parts by mass of alkanediol compound.

[0028] The peak area of an ether-containing dihydric alcohol appearing eight to fifteen minutes after the retention time of the main peak is preferably 0.3% or less, more preferably 0.2% or less, and still more preferably 0.15% or less of the peak area of the main peak. When the peak area of an ether-containing dihydric alcohol exceeds 0.3% of the main peak area, the content of the ether-containing dihydric alcohol exceeds 0.3 parts by mass per 100 parts by mass of alkanediol compound. This may cause a smell.

[0029] An alkanediol composition according to the present invention may be produced by any known method that can reduce an ester compound by-product to 0.005 parts by mass or less, and/or that can reduce a dioxane compound by-product to 0.2 parts by mass or less, per 100 parts by mass of alkanediol compound. As described above, the content of ester compound and/or the content of dioxane compound cannot be reduced to the range described above by common distillation alone. A smell therefore cannot be removed. This is probably because the boiling points of the components causing a smell, that is, an ester compound and a dioxane compound, are very close to the boiling point of the alkanediol compound.

[0030] Examples of a purification method used in the production of an alkanediol composition according to the present invention include azeotropic distillation of by-products and a large amount of water under reduced pressure; azeotropic distillation of by-products and an organic solvent under reduced pressure; azeotropic distillation of by-products, water, and an organic solvent under reduced pressure; blowing of water vapor under reduced pressure; adsorption of by-products on an adsorbent, such as an ion exchange resin or activated carbon, and subsequent distillation; recrystallization in a solvent, such as ethanol, acetone, or hexane; and combinations thereof; and combinations of these methods and known purification methods.

[0031] Among others, blowing of water vapor under reduced pressure; azeotropic distillation of by-products and water

and/or an organic solvent under reduced pressure (this is a method according to the present invention); and the addition of an organic solvent and blowing of water vapor under reduced pressure are preferred, because an ester compound causing a smell can efficiently be removed by these methods.

[0032] In the blowing of water vapor, the total amount of water is preferably in the range of 30 to 200 parts by mass, more preferably in the range of 50 to 150 parts by mass, and still more preferably in the range of 50 to 100 parts by mass per 100 parts by mass of alkanediol composition. The distillation temperature is preferably in the range of 80°C to 120°C, more preferably in the range of 85°C to 110°C, and still more preferably in the range of 90°C to 100°C. The degree of vacuum is preferably 10 kPa or less, more preferably 5 kPa or less, and still more preferably 1.3 kPa or less.

[0033] The amount of the organic solvent is preferably in the range of 30 to 200 parts by mass, more preferably in the range of 50 to 150 parts by mass, and still more preferably in the range of 80 to 120 parts by mass per 100 parts by mass of alkanediol composition. Furthermore, the organic solvent may be added in a plurality of portions. For example, the addition and removal of 10 parts by mass of organic solvent may be repeatedly performed. In the addition of the organic solvent in a plurality of portions, the total amount of the organic solvent is preferably in the range as described above.

[0034] The amount of water is preferably in the range of 30 to 200 parts by mass, more preferably in the range of 50 to 150 parts by mass, and still more preferably in the range of 80 to 120 parts by mass per 100 parts by mass of alkanediol composition. Furthermore, water may be added in a plurality of portions. For example, the addition and removal of 10 parts by mass of water may be repeatedly performed. In the addition of water in a plurality of portions, the total amount of water is preferably in the range as described above. The degree of vacuum is preferably 10 kPa or less, more preferably 5 kPa or less, and still more preferably 1.3 kPa or less.

[0035] When an organic solvent and water, or an organic solvent and water vapor, are combined, preferably 20-150 parts by mass, more preferably 30-100 parts by mass of water or water vapor per 100 parts by mass of organic solvent is added or blown. The total amount of the organic solvent and water or the total amount of the organic solvent and water vapor is preferably in the range of 50 to 300 parts by mass, more preferably in the range of 80 to 250 parts by mass, and still more preferably in the range of 100 to 200 parts by mass per 100 parts by mass of alkanediol composition. The degree of vacuum is preferably 10 kPa or less, more preferably 5 kPa or less, and still more preferably 1.3 kPa or less.

[0036] Examples of organic solvent for use in the purification method include glycol compounds, such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, methyl cellosolve, ethyl cellosolve, propyl cellosolve, butyl cellosolve, propylene glycol monomethyl ether, and diethylene glycol monomethyl ether; acyclic hydrocarbons, such as hexane, octane, nonane, and decane; and aromatic hydrocarbons, such as benzene, toluene, xylene, trimethylbenzene, cumene, and naphthalene. Among others, in terms of removal of by-products, glycol solvents are preferred, propylene glycol, dipropylene glycol, and diethylene glycol are more preferred, and propylene glycol is most preferred.

[0037] If necessary, another component may be added to an alkanediol composition according to the present invention within the limits not compromising the advantages of the present invention. Examples of the additive component include water; surfactants, such as nonionic surfactants, anionic surfactants, cationic surfactants, and amphoteric surfactants; antioxidants; light stabilizers; silicone oils; thickeners; oil solutions; powders (pigments, dyes, and resins); preservatives; perfumes; humectants; bioactive components; salts; solvents; antioxidants; chelating agents; counteractives; pH adjusters; enzymes; and cyclic oligosaccharides such as cyclodextrins.

[0038] An alkanediol composition according to the present invention may be allowed to react with another compound reactive with a hydroxyl group. Examples of the compound reactive with a hydroxyl group include isocyanate compounds, epoxy compounds, and compounds containing carboxylic acids such as fatty acids. An alkanediol composition according to the present invention may be allowed to react with these compounds and thereby be included in urethane resins, epoxy resins, and polyesters. Furthermore, because an alkanediol composition according to the present invention contains only a small amount of by-products, few side reactions occur, and a final product advantageously contains only a small amount of by-products.

[0039] A cosmetic according to the present invention contains an alkanediol composition according to the present invention. In the cosmetic, the alkanediol composition may be used as a humectant or a preservative, or a pearling agent in a shampoo. Examples of the cosmetic include facial cleansing creams, cleansing foams, cleansing creams, cleansing milks, cleansing lotions, massage creams, cold creams, moisture creams, sun blocks, body shampoos, hair shampoos, hair rinses, hair treatments, hair-restorers, hair creams, hair lacquers, setting lotions, hair bleaches, color rinses, permanent wave lotions, hand creams, lipsticks, packs, foundations, toilet water, cosmetic liquid, milky lotions, colognes, bath cosmetics, kitchen detergents, laundry detergents, bath detergents, nail cosmetics, and tooth powders.

EXAMPLES

[0040] The present invention will be further illustrated with examples below.

Production of diol compound

Production Example 1 (Production of octanediol)

[0041] 381 g (3.4 mol) of α-olefin having eight carbon atoms and 218 g (4.5 mol) of 95% formic acid were charged into a 2000 ml four-neck glass flask with a stirrer, a thermometer, and a nitrogen inlet. Then, 261 g (4.6 mol) of 60% hydrogen peroxide was added dropwise at 60°C for two hours. After the completion of dropping, the reactant was aged at 60°C for eight hours. After the reactant was left to stand and a lower aqueous layer was removed, 192 g (1.2 mol) of 25% aqueous sodium hydroxide was added to the reactant. The reactant was stirred at 60°C for 30 minutes for saponification and was left to stand. A lower aqueous layer was then removed. After the saponification and removal of the aqueous layer were performed one more time, the product was washed with hot water and hexane to yield 380 g of 1,2-octanediol.

Production Example 2 (Production of decanediol)

[0042] As in Production Example 1, 1,2-decanediol was produced from an α-olefin having 10 carbon atoms.

Production Example 3 (Production of dodecanediol)

[0043] As in Production Example 1, 1,2-dodecanediol was produced from an α-olefin having 12 carbon atoms. Purification

Treatment 1

[0044] A hundred grams of diol compound produced in Production Example 1, 2, or 3 and 100 g of propylene glycol were charged into a 500 ml four-neck glass flask with a stirrer, a thermometer, and a nitrogen inlet. The reactant was heated to 90°C to 95°C. Propylene glycol was then completely removed at a reduced pressure of 1.33 kPa to yield a purified diol compound.

Treatment 2

[0045] A hundred grams of diol compound produced in Production Example 1, 2, or 3, 100 g of propylene glycol, and 50 g of water were charged into a 500 ml four-neck glass flask with a stirrer, a thermometer, and a nitrogen inlet. The reactant was heated to 90°C to 95°C. Propylene glycol was then completely removed at a reduced pressure of 1.33 kPa to yield a purified diol compound.

Treatment 3

[0046] A hundred grams of diol compound produced in Production Example 1, 2, or 3 was charged into a 300 ml four-neck glass flask with a stirrer, a thermometer, and a nitrogen inlet. The reactant was distilled at a temperature in the range of 120°C to 180°C and a reduced pressure in the range of 1.4 to 1.8 kPa to yield a purified diol compound as a main fraction. Treatment 4

[0047] Fifty grams of diol compound produced in Production Example 1, 2, or 3 and 10 g of activated carbon were charged into a 200 ml beaker and were stirred at 50°C. After two hours, the activated carbon was filtered out to yield a purified diol compound.

[0048] The purified diol compounds thus produced were analyzed by gas chromatography under conditions described below. Peak areas were calculated to determine the amounts of impurities. The amounts of impurities were expressed as ratios of peak area to that of the main peak (diol compound), which was set to be 100. Tables 1 to 3 show the results for 1,2-octanediol (Production Example 1), 1,2-decanediol (Production Example 2), and 1,2-dodecanediol (Production Example 3), respectively.

Analyzer: GC-14B (Shimadzu Corporation)
Column: DB-1 (J & W Scientific, 100% dimethylpolysiloxane, inner diameter 0.53 mm, length 15 m, film thickness 1.5 μm)
Carrier gas: Nitrogen, 20 ml/min
Air pressure: 50 kPa
Hydrogen pressure: 50 kPa
Temperature of vaporization chamber: 320°C
Heating rate: held at 60°C for five minutes, heated to 280°C at 10°C/min, and held at 280°C for three minutes.

[0049] Sample amount: 0.1 μl (1.5% by weight in ethanol)

Table 1

	Retention time (min)				
	8.3~10.2	10.3	10.4~12.3	14.3~17.3	18.3~25.3
Treatment 1	0.003	100	0	0.16	0.29
Treatment 2	0.001	100	0	0.03	0.25
Treatment 3	0.03	100	0	0.29	0.41
Treatment 4	0.13	100	0	0.32	0.48
Untreated	0.25	100	0.05	0.48	0.58
Identified components	Ester compound	Diol compound	-	Dioxane compound	Ether-containing dihydric alcohol

Table 2

	Retention time (min)				
	11.1~13.0	13.1	13.2~15.1	17.1~20.1	21.1~28.1
Treatment 1	0.006	100	0	0.18	0.32
Treatment 2	0.002	100	0	0.04	0.23
Treatment 3	0.05	100	0	0.30	0.42
Treatment 4	0.14	100	0	0.33	0.51
Untreated	0.23	100	0.04	0.46	0.61
Identified components	Ester compound	Diol compound	-	Dioxane compound	Ether-containing dihydric alcohol

Table 3

	Retention time (min)				
	13.7~15.6	15.7	15.8~17.7	19.7~22.7	23.7~30.7
Treatment 1	0.006	100	0	0.19	0.29
Treatment 2	0.002	100	0	0.06	0.21
Treatment 3	0.05	100	0	0.25	0.41
Treatment 4	0.15	100	0	0.32	0.49
Untreated	0.21	100	0.03	0.45	0.6
Identified components	Ester compound	Diol compound	-	Dioxane compound	Ether-containing dihydric alcohol

Test Example 1

[0050] Alkanediol compounds in Treatments 1 to 4 and untreated alkanediol compounds were evaluated by ten panelists (five men and five women) for evaluation items described below. Table 4 shows the results.

O: No smell.
Δ: A little smell but not unpleasant.
×: Unpleasant smell.

Table 4

		Number of Panelists		
		○	Δ	×
Treatment 1	1,2-octanediol	9	1	0
	1,2-decanediol	8	2	0
	1,2-dodecanediol	9	1	0
Treatment 2	1,2-octanediol	10	0	0
	1,2-decanediol	10	0	0
	1,2-dodecanediol	10	0	0
Treatment 3	1,2-octanediol	0	4	6
	1,2-decanediol	0	3	7
	1,2-dodecanediol	0	4	6
Treatment 4	1,2-octanediol	0	2	8
	1,2-decanediol	0	1	9
	1,2-dodecanediol	0	1	9
Untreated	1,2-octanediol	0	0	10
	1,2-decanediol	0	0	10
	1,2-dodecanediol	0	0	10

[0051] These results show that, in gas chromatography, a large peak (ester compound) at zero to two minutes before the peak of a diol compound and/or a large peak (dioxane compound) at four to seven minutes after the peak of the diol compound are indicative of an unpleasant smell.

Test Example 2

[0052] 1,2-octanediol in Production Example 1 was purified by the method described in Treatment 2. Shampoos were prepared with the purified 1,2-octanediol and untreated 1,2-octanediol according to the formula shown in Table 5. The two shampoos were evaluated by ten panelists (five men and five women) for smell when the shampoos were used.

Table 5

Component	Amount (% by mass)
Sodium polyoxyethylene (3) lauryl ether sulfate	25.0
Lauryl amine oxide	3.0
Lauryl amine propyl betaine	18.0
Propylene glycol	3.2
Hydroxyethyl cellulose	0.5

(continued)

Component	Amount (% by mass)
1,2-octanediol	0.1
Purified water	Remainder

[0053] As a result of evaluating the smell of shampoo, nine panelists felt that the smell of the shampoo containing a 1,2-octanediol composition purified by the method described in Treatment 2 was better than that of the shampoo containing an untreated 1,2-octanediol composition; one panelist felt that the two shampoos have the same smell; and no panelist felt that the smell of the shampoo containing an untreated 1,2-octanediol composition was better than that of the shampoo containing a purified 1,2-octanediol composition.

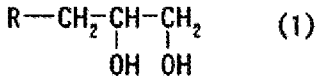
Claims

1. An alkanediol composition comprising 0.005 parts by mass or less of ester compound (A) per 100 parts by mass of alkanediol compound having four or more carbon atoms.

2. An alkanediol composition comprising 0.2 parts by mass or less of dioxane compound (C) per 100 parts by mass of alkanediol compound having four or more carbon atoms.

3. The alkanediol composition according to Claim 1 or 2, further comprising 0.3 parts by mass or less of ether-containing dihydric alcohol (B) per 100 parts by mass of the alkanediol compound.

4. The alkanediol composition according to any one of Claims 1 to 3, wherein the alkanediol compound has a general formula (1):



(1)

wherein R denotes an alkyl group having 4-15 carbon atoms.

5. The alkanediol composition according to any one of Claims 1 to 4, wherein the alkanediol compound is a hydrolysate of an epoxy compound produced by an oxidation reaction of an olefin.

6. A process for producing an alkanediol composition, comprising the steps of:

(a) oxidizing an olefin to produce an epoxy compound;
(b) hydrolyzing the epoxy compound to produce the alkanediol composition; and
(c) adding water and/or an organic solvent to the alkanediol composition and removing water and/or the organic solvent under reduced pressure.

7. A cosmetic comprising the alkanediol composition according to any one of Claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/308652

A. CLASSIFICATION OF SUBJECT MATTER
C07C29/10(2006.01), ***A61K8/30***(2006.01), ***C07C29/80***(2006.01), ***C07C31/20***(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C29/10(2006.01), ***A61K8/30***(2006.01), ***C07C29/80***(2006.01), ***C07C31/20***(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2000-505103 A (LG Chemical Ltd.), 25 April, 2000 (25.04.00), Table 6 & US 6201159 B1 & WO 98/017614 A1	2-3 1
X Y A	JP 61-65834 A (Daicel Chemical Industries, Ltd.), 04 April, 1986 (04.04.86), Claims; page 1, lower right column, lines 3 to 9; example 1 (Family: none)	2-3,7 6 1
Y A	JP 7-10789 A (Daicel Chemical Industries, Ltd.), 13 January, 1995 (13.01.95), Claim 1 & US 5345004 A & EP 616992 A1	6 1

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 May, 2006 (17.05.06)	30 May, 2006 (30.05.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/308652

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 61-130247 A (Degussa AG.), 18 June, 1986 (18.06.86), Claim 1 & US 4605795 A & EP 183029 A2 & DE 3442937 A1	6 5
A	JP 2004-115404 A (Kyowa Yuka Co., Ltd.), 15 April, 2004 (15.04.04), Par. Nos. [0009], [0019] (Family: none)	4,7

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 57062234 A **[0005]**
- JP 60078928 A **[0006]**

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NOTICE OF ALLOWANCE AND FEE(S) DUE

171052 7590 09/11/2020

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1200 19th St. NW
Washington, DC 20036

EXAMINER
CUTLIFF, YATE KAI RENE

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 09/11/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	12/11/2020

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(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	12/11/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

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NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

171052 7590 09/11/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

EXAMINER	
CUTLIFF, YATE KAI RENE	
ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 09/11/2020

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/262,898	Applicant(s) Burgo et al.	
	Examiner YATE K CUTLIFF	Art Unit 1622	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to RCE of 8/21/2020.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-34 and 88-91 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 8/21/2020.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Continued Examination Under 37 CFR 1.114

2. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after allowance or after an Office action under *Ex Parte Quayle*, 25 USPQ 74, 453 O.G. 213 (Comm'r Pat. 1935). Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, prosecution in this application has been reopened pursuant to 37 CFR 1.114. Applicant's submission filed on August 21, 2020 has been entered.

Information Disclosure Statement

3. The information disclosure statement (IDS) submitted on August 21, 2020 was filed after the mailing date of the Notice of Allowance on May 21, 2020. The submission is in compliance with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

4. The information disclosure statement (IDS) submitted on August 21, 2020 incorrectly listed the Name of Patentee or Applicant in the U.S. Patent Application Publications section of the IDS. Cite No. 4 list the name as “Swern”; however, the name associated with U.S. Pat. Appl. No. 2016/0161025 is Osterholt et al.. The Examiner corrected the name on the IDS to reflect the correct Name of the Patentee or Applicant at Cite No. 4.

Allowable Subject Matter

5. Claims 1 – 34 and 88 – 91 are allowed.

6. The following is an examiner's statement of reasons for allowance: Claims are allowed for reasons of record set out in the Notice of Allowance mailed April 13, 2020.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to YATE K. CUTLIFF whose telephone number is (571)272-9067. The examiner can normally be reached on Monday-Friday (8:30 - 5:30).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf can be reached on (571) 272 - 2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for

published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see https://ppair-my.uspto.gov/pair/PrivatePair. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020	05/18/2020	09/08/2020					
	1	✓	=	=	=					
	2	✓	=	=	=					
	3	✓	=	=	=					
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	41	✓	-	-	-					
	42		-	-	-					

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020	05/18/2020	09/08/2020					
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	89		=	=	=					
	90		=	=	=					
	91		=	=	=					

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC								
Symbol							Type	Version
C07C	/	29	/	04			F	2013-01-01
C07C	/	31	/	20			I	2013-01-01
C07C	/	29	/	80			I	2013-01-01
B01J	/	23	/	06			I	2013-01-01
B01J	/	37	/	08			I	2013-01-01
B01J	/	21	/	04			I	2013-01-01
C11D	/	3	/	2044			I	2013-01-01
C07C	/	1	/	24			I	2013-01-01
C07C	/	29	/	48			I	2013-01-01
C07C	/	11	/	02			I	2013-01-01
C07C	/	11	/	107			I	2013-01-01
B01J	/	2523	/	27			A	2013-01-01
C07B	/	41	/	02			A	2013-01-01
C07B	/	63	/	00			A	2013-01-01
B01J	/	2523	/	31			A	2013-01-01
A61L	/	2	/	18			A	2013-01-01
A01N	/	31	/	02			A	2013-01-01
A61K	/	8	/	345			A	2013-01-01
A61Q	/	5	/	00			A	2013-01-01
A61Q	/	11	/	00			A	2013-01-01
A61Q	/	19	/	00			A	2013-01-01
C11D	/	3	/	48			A	2013-01-01
C07C	/	2521	/	04			A	2013-01-01

CPC Combination Sets									
Symbol							Type	Set	Ranking	Version
C07C	/	1	/	24			I	1	1	2013-01-01
C07C	/	11	/	02			I	1	2	2013-01-01
C07C	/	29	/	48			I	2	1	2013-01-01
C07C	/	31	/	20			I	2	2	2013-01-01

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	08 September 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office — Part of Paper No.: 20200908

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CPC Combination Sets												
Symbol						**Type**	**Set**	**Ranking**	**Version**
C07C	/	29	/	80		I	3	1	2013-01-01
C07C	/	31	/	20		I	3	2	2013-01-01

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	08 September 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

INTERNATIONAL CLASSIFICATION					
CLAIMED					
C07C	/	29	/	04	
C07C	/	29	/	48	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	08 September 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	13	13	25	25		37		49		61		73		85
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3	3	15	15	27	27		39		51		63		75		87
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5	5	17	17	29	29		41		53		65		77	36	89
6	6	18	18	30	30		42		54		66		78	37	90
7	7	19	19	31	31		43		55		67		79	38	91
8	8	20	20	32	32		44		56		68		80		
9	9	21	21	33	33		45		57		69		81		
10	10	22	22	34	34		46		58		70		82		
11	11	23	23		35		47		59		71		83		
12	12	24	24		36		48		60		72		84		

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	08 September 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

U.S. Patent and Trademark Office Part of Paper No.: 20200908

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC - Searched*		
Symbol	Date	Examiner
C07C 29/04, 48	09/08/2020	ykc
C07C 31/20	09/08/2020	ykc
C07C 33/025	09/08/2020	ykc
C07C 2521/04	04/03/2020	ykc
B01J 21/04	09/08/2020	ykc
B01J 23/06	09/08/2020	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	04/03/2020	ykc
C07B 41/02	04/03/2020	ykc

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

Search Notes		
Search Notes	**Date**	**Examiner**
Palm Inventor Search	09/08/2020	ykc
East	09/08/2020	ykc
C07C 29/04, 48	09/08/2020	ykc
C07C 31/20	09/08/2020	ykc
C07C 33/025	09/08/2020	ykc
C07C 2521/04	05/18/2020	ykc
B01J 21/04	09/08/2020	ykc
B01J 23/06	09/08/2020	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	05/18/2020	ykc
C07B 41/02	05/18/2020	ykc

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
C07C	29/04, 48	09/08/2020	ykc
C07C	31/20	09/08/2020	ykc
C07C	33/025	09/08/2020	ykc
B01J	21/04	09/08/2020	ykc
B01J	23/06	09/08/2020	ykc

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16262898
Filing Date	2019-01-30
First Named Inventor	Rocco V. Burgo
Art Unit	1622
Examiner Name	CUTLIFF, YATE KAI RENE
Attorney Docket Number	INLX.0198U1/484809

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
/Y.K.C/	1	4234752		1980-11-18	Yulin Wu	
/Y.K.C/	2	8912373	B2	2014-12-16	Michael Wright	
/Y.K.C/	3	9856461	B2	2018-01-02	Jeffrey Fortman	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
/Y.K.C/	1	20140066666	A1	2014-03-06	Oskar Koch	
/Y.K.C/	2	20050065389	A1	2005-03-24	De Bruyn	
/Y.K.C/	3	20030065233	A1	2003-04-03	Fuji	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

/Y.K.C/	4	20060161025	A1	2008-06-10	Swern Osterholt et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
/Y.K.C/	1	1876162	EP	A1	2008-01-09	Furuya		

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
/Y.K.C/	1	Wang et al., Efficient conversion of microcrystalline cellulose to 1,2-alkanediols over supported Ni catalysts, GREEN CHEM., 14:758-765 (2012)	
/Y.K.C/	2	Jong & Birmingham, Mushrooms as a Source of Natural Flavor and AromaCcompouds", Chapter 37 (pp. 345-366) in MUSHROOM BIOLOGY AND MUSHROOM PRODUCTS (Chinese University Press 1993)	
/Y.K.C/	3	Swern et al., Hydroxylation and Epoxidation of Some 1-Olefins with Per-acids, JACS, 68:1504-1507 (1946)	
/Y.K.C/	4	Klug et al., Degradation of Hydrocarbons by Members of the Genus Candida, II. Oxidation of n-Alkanes and 1-Alkenes by Candida lipolytica, Journal of Bacteriology, Vol. 93, No. 6, pp 1847-1852 (1964)	
/Y.K.C/	5	Liu et al., Hydrogen peroxide-independent production of α-alkenes by OleTJE P450 fatty acid decarboxylase, Biotechnology for Biofuels, 7:28 (2014)	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

EXAMINER SIGNATURE			
Examiner Signature	/YATE' K CUTLIFF/	Date Considered	09/08/2020

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:57
S2	69	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S3	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S4	69	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S5	2	"2016007196".pn.	US-PGPUB; USPAT; USOCR; FPRS; EPO	OR	OFF	2019/07/31 11:33
S6	9,189	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:43
S7	1,392	(natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:45
S8	23	S6 and S7 and alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 12:46
S9	9,170	(method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S10	684	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and dehydration	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S11	378	S10 and (natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:51

S12	125	S11 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:02
S13	125	S12 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:03
S14	9,170	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S15	1,219	S14 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:05
S16	1,175	S15 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S17	55	S14 and (terminal with (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:07
S18	3	("20050006997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:29
S19	3	("20050069997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:30
S20	5,912	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:35
S21	2,221	S20 and (natural or plant or vegetable or ferment$4 or biomass)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:40
S22	312	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and (peracid or	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42

		formic of acetic) and (hydrogen adj peroxide)				
S23	308	S22 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S24	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:51
S25	3,031	C07C29/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:15
S26	5,809	C07C31/20.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S27	0	C07C33/25.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S28	3,127	C07C33/025.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S29	18,997	B01J21/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S30	16,230	B01J37/08.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:18

S31	4,501	B01J23/06.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:21
S32	14,742	c07c2521/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:22
S33	38	S25 and S28	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:23
S34	2	S20 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:24
S35	5	S28 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:25
S36	0	S25 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S37	0	S33 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S38	1	"7385092".pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 16:49
S39	1	"20170360035".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/08/01 10:10

S40	13	(biodiene? or (bio adj diene?) or (bio adj alkene) or bioalkene)	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/08/01 10:27
S41	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:13
S42	27	S41 and hydrolysis	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:13
S43	9,195	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:16
S44	886	S43 and hydrolysis	USPAT	OR	OFF	2019/08/01 11:16
S45	24	S43 and hydrolysis and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:17
S46	5	S43 and (hydroxide with hydrolysis) and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:24
S47	1	"20140066666".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:26
S48	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:29
S49	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:30
S50	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S51	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S52	2,015	c07c29/48.cpc.	US-PGPUB; USPAT; USOCR;	OR	OFF	2020/04/03 12:49

			FPRS; EPO; JPO; DERWENT; IBM_TDB			
S53	1,075	c07b41/02.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:54
S54	24,629	c07c11/02,107.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S55	32	S53 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S56	9	S55 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S57	23	S52 and S53	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S58	5	S57 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S59	48	S52 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:58
S60	6	S59 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO;	OR	OFF	2020/04/03 12:58

			JPO; DERWENT; IBM_TDB			
S77	13	("20050006997," "20060161025," "20160090331," "20170360035," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 11:20
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S80	3	S78 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 11:50
S81	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/05/18 12:03
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S84	5	S83 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 12:23
S85	8	("2004078336," "2013077904," "2013106065," "105312044").pn.	FPRS; EPO	OR	OFF	2020/05/18 12:25
S86	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:28

S87	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S88	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S89	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S104	7	("20030065233" | "20050065389" | "20060161025" | "20140066666" | "4234752" | "8912373" | "9856461").PN.	US-PGPUB; USPAT	OR	OFF	2020/09/08 10:08
S105	124	((swern) near (daniel)).inv.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/09/08 10:33
S106	116	((swern) near (daniel)).inv.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 10:34
S107	1	"20080161025".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 10:38
S108	1	"20070161025".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 10:39
S109	9,940	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 10:40
S110	1	S104 and S109	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/09/08 10:40
S111	7	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:13
S112	72	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:14
S113	3	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:14
S114	73	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:14
S115	25	bio near2 alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:16
S116	17	bio adj alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:17
S117	5	S115 and (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:23

S118	154	1-alkene and (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:23
S119	149	S118 and @ay<="2017"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/09/08 12:24
S120	16	1-alkene same (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:41

EAST Search History (Interference)

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S63	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S64	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S65	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S66	698	C07C31/20.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S67	251	c07c29/48.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S68	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S69	3,196	c07c11/02,107.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S70	2,105	B01J21/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S71	2,140	c07c2521/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S72	2	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S69	USPAT	OR	OFF	2020/04/03 13:07
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S74	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S65	USPAT	OR	OFF	2020/04/03 13:10
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S76	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S68	USPAT	OR	OFF	2020/04/03 13:10
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S93	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/05/18 12:41
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S95	2,128	B01J21/04.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S96	2,151	c07c2521/04.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S97	2	(S90 or S91 or S92) and S94 and (S95 or S96) and S94	USPAT	OR	OFF	2020/05/18 12:41
S98	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/05/18 12:43
S99	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S98	USPAT	OR	OFF	2020/05/18 12:43
S100	2	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S94	USPAT	OR	OFF	2020/05/18 12:43
S101	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S98	USPAT	OR	OFF	2020/05/18 12:44
S102	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/05/18 12:44
S103	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S102	USPAT	OR	OFF	2020/05/18 12:44
S121	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/09/08 12:51
S122	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/09/08 12:51
S123	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/09/08 12:52
S124	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/09/08 12:52
S125	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/09/08 12:59

S126	415	C07C29/04.cpc.	USPAT	OR	OFF	2020/09/08 12:59
S127	689	C07C31/20.cpc.	USPAT	OR	OFF	2020/09/08 13:00
S128	401	C07C33/025.cpc.	USPAT	OR	OFF	2020/09/08 13:01
S129	2,166	B01J21/04.cpc.	USPAT	OR	OFF	2020/09/08 13:01
S130	514	B01J23/06.cpc.	USPAT	OR	OFF	2020/09/08 13:02
S131	0	(S121 or S122 or S123 or S124) and S126 and S129	USPAT	OR	OFF	2020/09/08 13:02
S132	0	(S121 or S122 or S123 or S124) and S126 and S130	USPAT	OR	OFF	2020/09/08 13:03
S133	0	(S121 or S122 or S123 or S124) and S127 and S129	USPAT	OR	OFF	2020/09/08 13:03
S134	0	(S121 or S122 or S123 or S124) and S127 and S130	USPAT	OR	OFF	2020/09/08 13:03
S135	0	(S121 or S122 or S123 or S124) and S128 and S129	USPAT	OR	OFF	2020/09/08 13:03
S136	0	(S121 or S122 or S123 or S124) and S128 and S130	USPAT	OR	OFF	2020/09/08 13:03
S137	261	c07c29/48.cpc.	USPAT	OR	OFF	2020/09/08 13:17
S138	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S139	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S140	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S141	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S142	0	(S138 or S139 or S140 or S141) and S137	USPAT	OR	OFF	2020/09/08 13:18

9/8/2020 1:19:06 PM
C:\Users\ycutliff\Documents\EAST\Workspaces\16262898.wsp

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

BIB DATA SHEET

CONFIRMATION NO. 3410

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
16/262,898	01/30/2019	568	1622	INLX.0198U1/484809

APPLICANTS

Inolex Investment Corporation, Wilmington, DE

INVENTORS

Rocco V. Burgo, Mullica Hill, NJ;
Michael E. Wright, Hurricane, UT;
Gary B. Mosser, Tabernacle, NJ;
Michael J. Fevola, Belle Mead, NJ;

**** CONTINUING DATA ***************************

This appln claims benefit of 62/623,985 01/30/2018

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

02/15/2019

Foreign Priority claimed	❑ Yes ☑ No	❑ Met after Allowance	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
35 USC 119(a-d) conditions met	❑ Yes ☑ No		NJ	7	41	3
Verified and Acknowledged	/YATE KAI RENE CUTLIFF/ Examiner's Signature	Initials				

ADDRESS

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036
UNITED STATES

TITLE

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

FILING FEE RECEIVED		
3980	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	❑ All Fees ❑ 1.16 Fees (Filing) ❑ 1.17 Fees (Processing Ext. of time) ❑ 1.18 Fees (Issue) ❑ Other _____ ❑ Credit

Corrected Notice of Allowance - Correction of Issue Fee Amount

Due to a technical problem, the Notice of Allowance and Fee(s) Due mailed in this application specified an incorrect fee amount (the amount effective on October 2, 2020 for Notices of Allowance mailed on or after October 2, 2020). Corrected Notices of Allowance are being mailed to all applicants who are affected. This is necessary because the statute requires the applicant to pay the fee that is specified on the Notice of Allowance.

A Corrected Notice of Allowance is attached which specifies the correct issue fee. The time period for payment of the issue fee set forth in the previous Notice of Allowance and Fee(s) Due is being restarted to run THREE MONTHS from the "DATE MAILED" of the attached Corrected Notice of Allowance. Failure to timely comply will result in ABANDONMENT of this application. THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

For applicants who replied prior to receiving the Corrected Notice of Allowance:

Applicant must still file a completed Part B – Fee(s) Transmittal, Form PTOL-85 Part B, or an equivalent, in reply to the Corrected Notice of Allowance since the Corrected Notice of Allowance sets forth a time period for reply. This applies to those situations in which applicant's reply was not processed before the Corrected Notice of Allowance was mailed (e.g., the reply crossed in the mail with the Corrected Notice of Allowance) and those situations in which applicant's reply was already processed. Applicants should check the appropriate box in section 4b of Form PTOL-85 Part B, such as the box authorizing the Director to "charge the required fee(s), any deficiency, or credit any overpayment" to a deposit account number. If this box is checked, the applicant will be refunded the amount of any overpayment to the designated deposit account. In addition, by checking the appropriate box in section 4b of Form PTOL-85, Part B, the applicant requests the Office to "first reapply any previously paid fee shown above," as stated on the form. Applicant may also include an explanatory cover letter, if desired. If, however, applicant prefers to file an equivalent of Form PTOL-85, Part B, and if applicant paid an increased issue fee amount as specified on the Notice of Allowance, applicant may request a refund of the difference between the incorrect amount specified on the Notice of Allowance and the correct amount specified on the Corrected Notice of Allowance.

For questions regarding the issue fee amount calculation, please contact the Application Assistance Unit at 888-786-0101 or *HelpAAUCBuspto.gov*.

For assistance with PAIR or EFS-Web, please contact the Patent EBC at 1-866-217-9197 or *ebc@uspto.gov*.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

CORRECTED
NOTICE OF ALLOWANCE AND FEE(S) DUE

171052 7590 09/23/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

EXAMINER
CUTLIFF, YATE KAI RENE

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 09/23/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
REGULAR	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	12/23/2020

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: **(571)-273-2885**

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

171052 7590 09/23/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date indicated below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
REGULAR	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	12/23/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,

(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____

2 _____

3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑Issue Fee ❑Publication Fee (if required) ❑Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29 — NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

❑ Applicant asserting small entity status. See 37 CFR 1.27 — NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

❑ Applicant changing to regular undiscounted fee status. — NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

171052 7590 09/23/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

EXAMINER	
CUTLIFF, YATE KAI RENE	

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 09/23/2020

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: **(571)-273-2885**

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

171052 7590 09/23/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date indicated below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
REGULAR	UNDISCOUNTED	$1000	$0.00	$0.00	$1000	12/23/2020

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,

(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 COZEN O'CONNOR
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: INOLEX INVESTMENT CORPORATION

(B) RESIDENCE: (CITY and STATE OR COUNTRY): WILMINGTON, DELAWARE

Please check the appropriate assignee category or categories (will not be printed on the patent): ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies .....

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 50-3111

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29 — NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

☐ Applicant asserting small entity status. See 37 CFR 1.27 — NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

☐ Applicant changing to regular undiscounted fee status. — NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Victor Castellucci/ Date October 15, 2020

Typed or printed name Victor Castellucci Registration No. 43,535

PTOL-85 Part B (08-18) Approved for use through 01/31/2020 OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Electronic Patent Application Fee Transmittal

Application Number:	16262898
Filing Date:	30-Jan-2019
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	Victor Jay Castellucci/Valerie Dotson
Attorney Docket Number:	INLX.0198U1/484809

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
UTILITY APPL ISSUE FEE	1501	1	1000	1000

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**1000**

Electronic Acknowledgement Receipt

EFS ID:	40849598
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	171052
Filer:	Victor Jay Castellucci/Valerie Dotson
Filer Authorized By:	Victor Jay Castellucci
Attorney Docket Number:	INLX.0198U1/484809
Receipt Date:	15-OCT-2020
Filing Date:	30-JAN-2019
Time Stamp:	09:36:13
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1000
RAM confirmation Number	E20200E036522182
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	INLX_0198U1_484809_Issue_Fee_Payment_Transmittal.pdf	1529548 a73c0f7d1ddad20d1d0502dd85d2c16e5c71db25	no	1
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30719 785a3728f5e92b908bb8ba0a351036915beea33f	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	1560267		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/30EFS (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
(Submitted Only via EFS-Web)

Application Number	16262898	Filing Date	2019-01-30	Docket Number (if applicable)	INLX.0198U1/484809	Art Unit	1622
First Named Inventor	Rocco V. Burgo			Examiner Name	CUTLIFF, YATE KAI RENE		

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

- ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____
- ☐ Other _____

☒ Enclosed

- ☐ Amendment/Reply
- ☒ Information Disclosure Statement (IDS)
- ☐ Affidavit(s)/ Declaration(s)
- ☐ Other _____

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____ (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

☒ **The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.**
The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 503111

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

☒ Patent Practitioner Signature

Applicant Signature

PTO/SB/30EFS (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
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Signature of Registered U.S. Patent Practitioner			
Signature	/Victor Castellucci/	Date (YYYY-MM-DD)	2020-10-30
Name	Victor Castellucci	Registration Number	43535

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16262898
Filing Date	2019-01-30
First Named Inventor	Rocco V. Burgo
Art Unit	1622
Examiner Name	CUTLIFF, YATE KAI RENE
Attorney Docket Number	INLX.0198U1/484809

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	8450543	B2	2013-05-28	PETERS, Matthew W.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20120282207	A1	2012-11-08	LUTZ, Patrick J.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

	1	Non-Final Office Action with a mailing date of September 17, 2020 issued in U.S. Patent Application No. 16/262,902 (Examiner - NANNETTE HOLLOMAN)
	2	Third Party Submission Under 37 CFR 1.290 filed in U.S. Patent Application No. 16/682,059 on September 8, 2020 by DANIEL ALTMAN
	3	Email communication from Practitioner R. James Balls to Practitioner Victor Castellucci concerning the alleged relevance of the prosecution file wrappers of U.S. Appl. No. 16/262,902 and U.S. Appl. No. 16/682,059.

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Victor Castellucci/	Date (YYYY-MM-DD)	2020-10-30
Name/Print	Victor Castellucci	Registration Number	43,535

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

US008450543B2

(12) **United States Patent**
Peters et al.

(10) **Patent No.: US 8,450,543 B2**
(45) **Date of Patent: May 28, 2013**

(54) **INTEGRATED METHODS OF PREPARING RENEWABLE CHEMICALS**

(75) Inventors: **Matthew W. Peters**, Highlands Ranch, CO (US); **Joshua D. Taylor**, Evergreen, CO (US); **David E. Henton**, Midland, MI (US); **Leo E. Manzer**, Wilmington, DE (US); **Patrick R. Gruber**, Longmont, CO (US); **Josefa M. Griffith**, Parker, CO (US); **Yassin Al Obaidi**, Somerset, KY (US)

(73) Assignee: **Gevo, Inc.**, Englewood, CO (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **12/986,918**

(22) Filed: **Jan. 7, 2011**

(65) **Prior Publication Data**

US 2011/0172475 A1 Jul. 14, 2011

Related U.S. Application Data

(60) Provisional application No. 61/293,459, filed on Jan. 8, 2010.

(51) **Int. Cl.**
C07C 1/24 (2006.01)

(52) **U.S. Cl.**
CPC ***C07C 1/24*** (2013.01)
USPC **585/240**; 585/242; 585/250; 585/252; 585/275; 585/257; 585/300; 585/241; 585/310; 585/314; 585/330; 585/379; 585/440

(58) **Field of Classification Search**
USPC 585/14, 240, 254, 303, 310, 324, 585/640, 647, 241, 242, 250, 252, 257, 275, 585/300, 314, 330, 379, 440; 44/385, 398, 44/403, 437; 208/142 145
See application file for complete search history.

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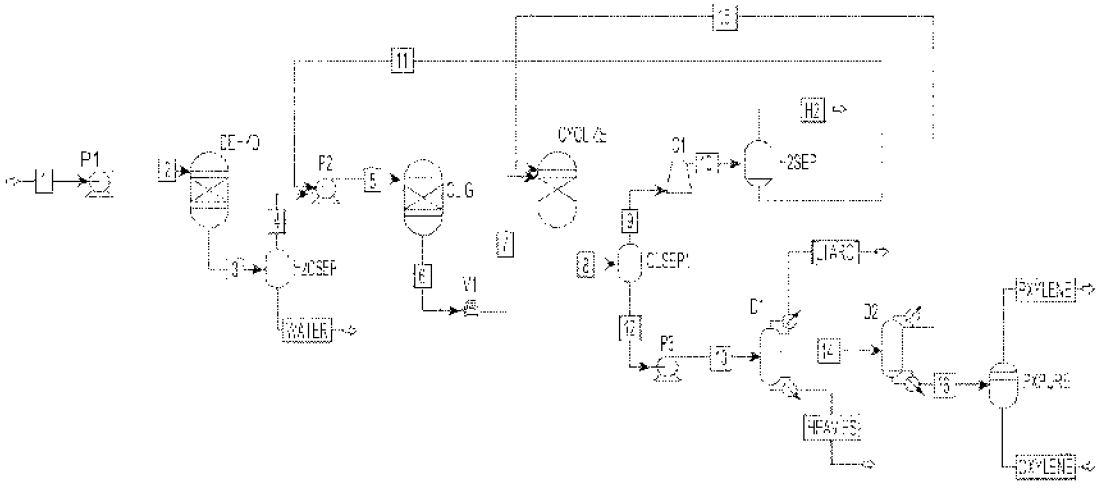
Primary Examiner In Suk Bullock
Assistant Examiner Sharon Pregler
(74) *Attorney, Agent, or Firm* Cooley LLP

(57) **ABSTRACT**

Isobutene, isoprene, and butadiene are obtained from mixtures of C_4 and/or C_5 olefins by dehydrogenation. The C_4 and/or C_5 olefins can be obtained by dehydration of C_4 and C_5 alcohols, for example, renewable C_4 and C_5 alcohols prepared from biomass by thermochemical or fermentation processes. Isoprene or butadiene can be polymerized to form polymers such as polyisoprene, polybutadiene, synthetic rubbers such as butyl rubber, etc. in addition, butadiene can be converted to monomers such as methyl methacrylate, adipic acid, adiponitrile, 1,4-butadiene, etc. which can then be polymerized to form nylons, polyesters, polymethylmethacrylate etc.

19 Claims, 5 Drawing Sheets



Integrated System to Convert Isobutanol to Renewable p-Xylene

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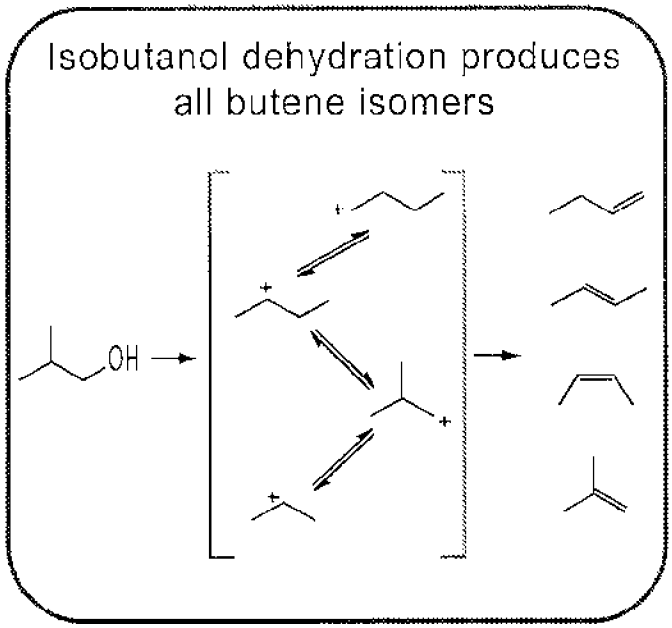
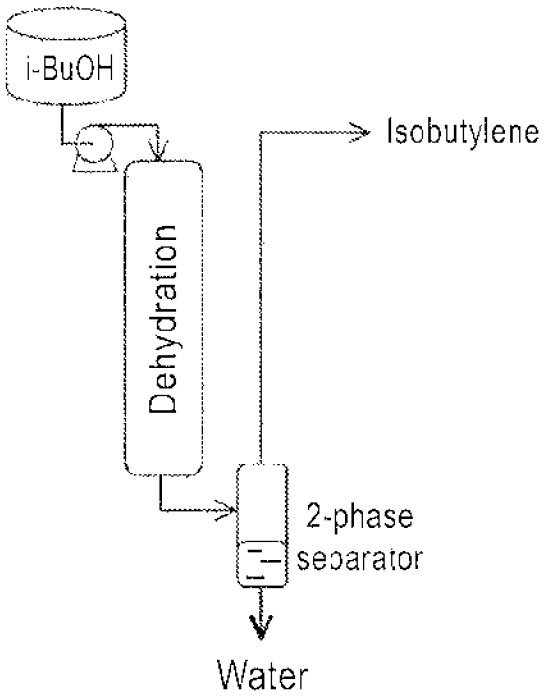


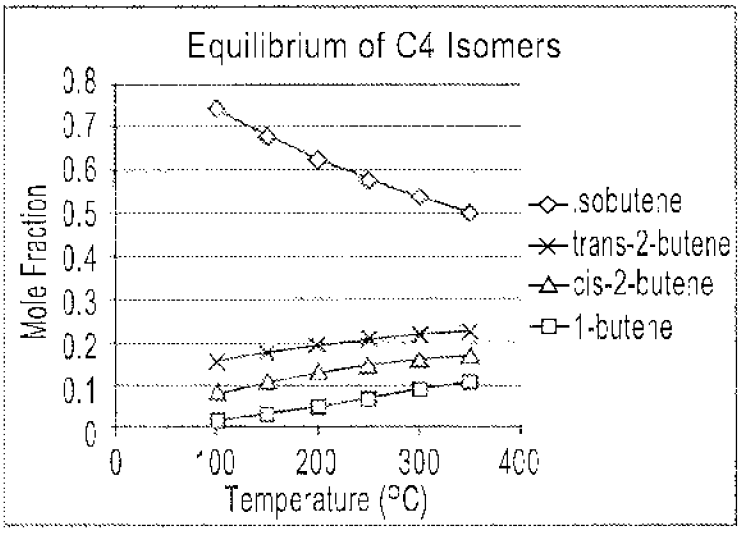
Dehydration of Isobutanol

Figure 1



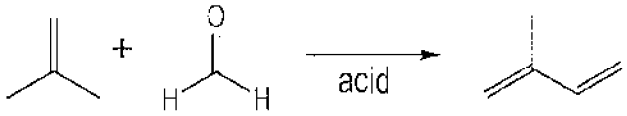
Dehydration Reactor Schematic

Figure 2



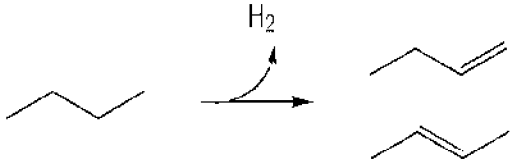
Equilibrium Composition of C_4 Isomers vs. Temp.

Figure 3



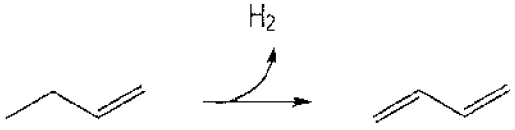
Isoprene via Prins Reaction

Figure 4



Dehydrogenation of n-butane

Figure 5



Dehydrogenation of 1-butene to 1,3-butadiene

Figure 6

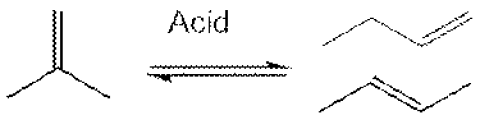


Figure 7: Skeletal Rearrangement of Isobutene

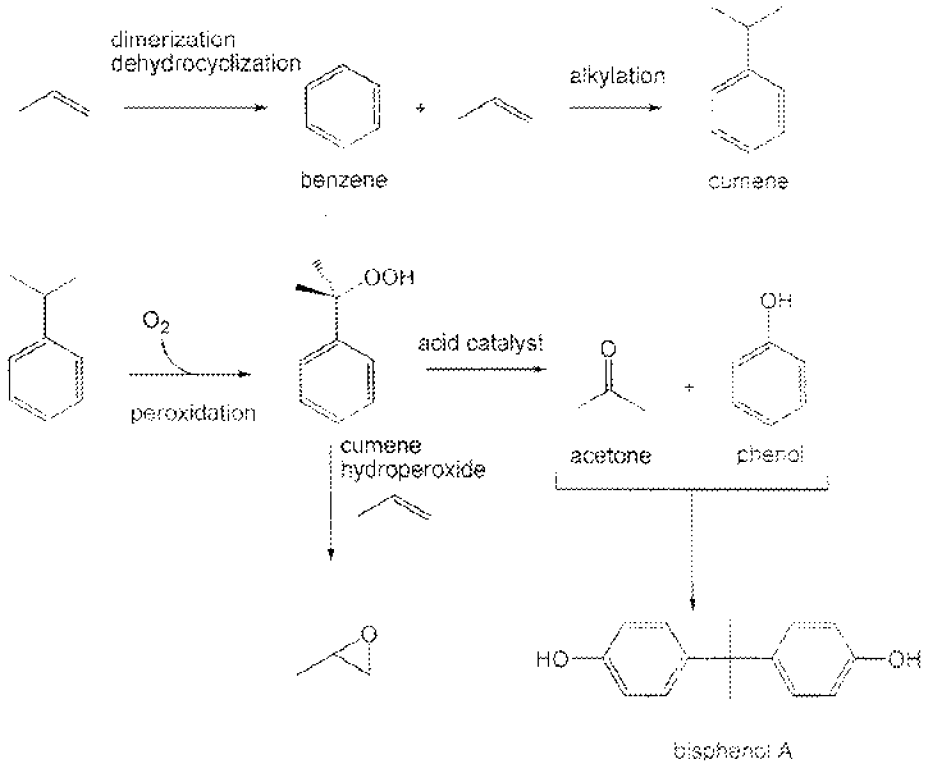
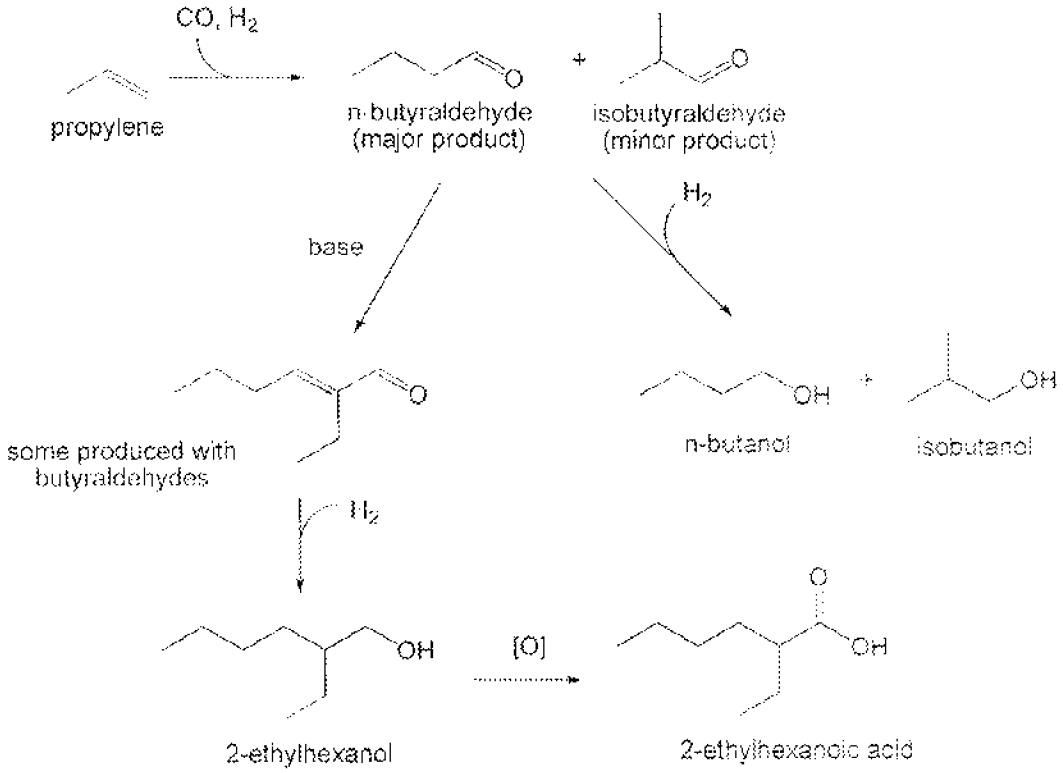


Figure 8


CO, H2
propylene
n-butyraldehyde
(major product)
isobutyraldehyde
(minor product)
base
H2
some produced with
butyraldehydes
n-butanol
isobutanol
H2
OH
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OH
2-ethylhexanol
2-ethylhexanoic acid

Figure 9

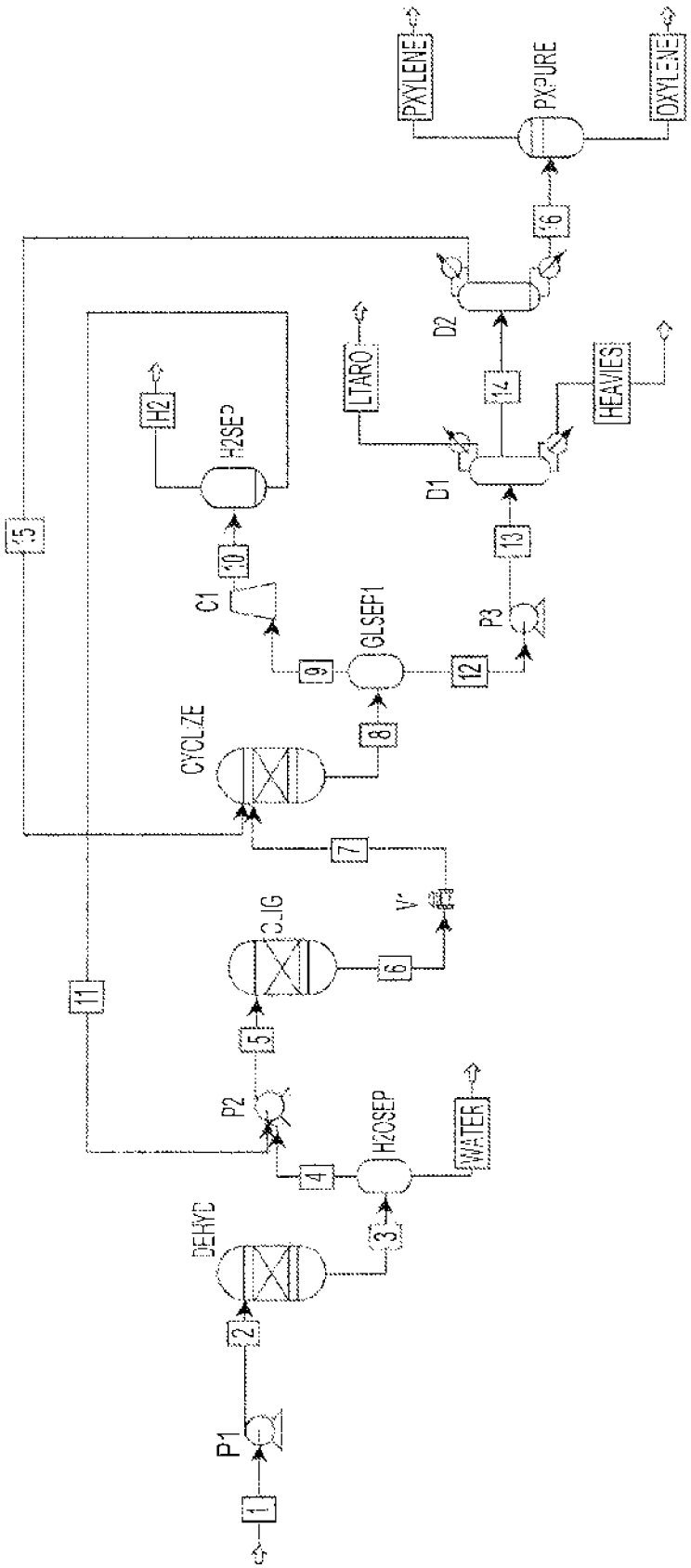


Figure 10

Integrated System to Convert Isobutanol to Renewable p-Xylene

INTEGRATED METHODS OF PREPARING RENEWABLE CHEMICALS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Appl. No. 61/293,459, filed Jan. 8, 2010, which is herein incorporated by reference in its entirety for all purposes.

BACKGROUND OF THE INVENTION

Conventional transportation fuels and chemicals (e.g., monomers, polymers, plasticizers, adhesives, thickeners, aromatic and aliphatic solvents, etc.) are typically derived from non-renewable raw materials such as petroleum. However, the production, transportation, refining and separation of petroleum to provide transportation fuels and chemicals is problematic in a number of significant ways.

For example, petroleum (e.g., crude oil and/or natural gas) production poses a number of environmental concerns. First, the history of petroleum production includes many incidents where there have been uncontrolled releases of crude petroleum during exploration and production (e.g., drilling) operations. While many of these incidents have been relatively minor in scale, there have been a number of incidents that have been significant in scale and environmental impact (e.g., BP's Deepwater Horizon incident, Mississippi Canyon, Gulf of Mexico, 2010).

World petroleum supplies are finite. Thus, as world petroleum demand has increased (84,337 M bpd worldwide in 2009; *US Energy Information Administration*), easily accessible reserves have been depleted. Accordingly, petroleum exploration and production operations are more frequently conducted in remote and/or environmentally sensitive areas (e.g., deepwater offshore, arctic regions, wetlands, wildlife preserves, etc.). Some remote locations require highly complex, technically challenging solutions to locate and produce petroleum reserves (e.g., due to low temperatures, water depth, etc.). Accordingly, the potential for large-scale environmental damage resulting from uncontrolled discharge of petroleum during such complex, technically challenging exploration and production operations is substantively increased.

In addition, when petroleum is produced in remote areas and/or areas which do not have infrastructure (e.g., refineries) to further process petroleum into useful products, the produced petroleum must be transported (e.g., via pipeline, rail, barge, ship, etc.), often over significant distances, to terminal points where the petroleum products may be refined and/or processed. Transportation of petroleum is also an operation with associated risk of accidental discharge of petroleum in the environment, with concomitant environmental damage, and there have been a number of significant incidents (e.g., Exxon's Valdez tanker spill, Prince William Sound, Ak., 1989). Furthermore, much of the world's proven petroleum reserves are located in regions which are politically unstable. Accordingly, supplies of petroleum from such regions may be uncertain since production of petroleum or transportation of petroleum products from such regions may be interrupted.

Petroleum is a complex mixture of chemical compounds. Crude petroleum comprises chemical entities from very the simple, e.g., helium and methane prevalent in natural gas, to the complex, e.g., asphaltenes and heterocyclic organic compounds prevalent in heavy, sour crude oil. Furthermore, crude petroleum is typically co-produced with varying amounts of formation water (e.g., water from the rock formation from which the petroleum was produced), often as stable emulsion, with salts, metals and other water-soluble compounds dissolved in the formation water. Crude oil may also contain varying amounts of particulate salts, metals, sediments, etc. Accordingly, crude oil streams are typically desalted, then allowed to settle and phase-separate into crude and water fractions, reducing the water content of the crude and the level of undesired components such as salts, metals, silt, sediment, etc. which may be present in the crude. Such undesired components are generally problematic in further processing and/or refining of petroleum into commercially useful fractions. For example, certain unit operations in the refining process may be sensitive to water, salt or sediment. Further, piping, storage and process vessels employed in the transport, storage and processing of petroleum is prone to corrosion, which may be accelerated and/or exacerbated by the presence of salt and/or water in the petroleum feedstock.

Desalting processes typically require the use of large quantities of water, which also may be heated, to extract salt and soluble metals from the crude oil. Further, the crude stream to be desalted is also generally heated to effect mixing with the extraction water. The resulting emulsions may then be treated with demulsifying agent and allowed to settle prior to further processing. Such desalting (and settling) may be time consuming, and may require (i) large quantities of water to extract the undesirable components, (ii) large amounts of energy to heat the water and/or crude stream(s) to effect mixing, and (iii) the use of substantial quantities of chemical agents to treat the crude (e.g., demulsifiers). As a result, large quantities of contaminated water are produced in desalting operation which must be treated to remove residual oil, dissolved salts, metals, water-soluble organics, demulsifiers, etc.

Furthermore, crude petroleum from regions, different subterranean reservoirs within a region, or even from different strata within a single field may have different chemical compositions. For example, crude oils can range from "light, sweet" oils which generally flow easily, and have a higher content of lower molecular weight hydrocarbons and low amounts of contaminants such as sulfur, to heavy, sour oils, which may contain a large fraction of high molecular weight hydrocarbons, large amounts of salts, sulfur, metals and/or other contaminants, and may be very viscous and require heating to flow. Furthermore, the relative amounts of the constituent fractions (e.g., light, low molecular weight hydrocarbons vs. heavier, higher molecular weight hydrocarbons) of the various grades or types of crude oil varies considerably. Thus, the chemical composition of the feedstock for a refinery may vary significantly, and as a result, the relative amounts of the hydrocarbon streams produced may vary as a function of the crude feed.

Once the crude feedstock is sufficiently treated to remove undesired impurities or contaminants, it can then be subject to further processing and/or refining. The crude feedstock is typically subject to an initial distillation, wherein the various fractions of the crude are separated into distillate fractions based on boiling point ranges. This is a particularly energy intensive process, as this separation is typically conducted on a vast scale, and most or all of the feedstock is typically heated in the distillation unit(s) to produce various distillate fractions. Furthermore, since the crude composition is quite complex, containing hundreds of compounds (if not more), each fraction may contain many different compounds, and the composition and yield of each distillate fraction may vary depending on the type and composition of crude feedstock. Depending on the desired product distribution on the back end of a refining operation, a number of additional refining

steps may be performed to further refine and/or separate the distillate streams, each of which may require additional equipment and energy input.

For example, higher boiling fractions from an initial distillation may be subject to further distillation (e.g., under vacuum) to separate the mixture even further. Alternatively, heavy fractions from an initial distillation may be subject to "cracking" (e.g., catalytic cracking) at high temperatures to reduce the average molecular weight of the components of the feed stream. Since lighter hydrocarbon fractions (e.g., containing less than 20 carbon atoms) generally have greater commercial value and utility than heavier fractions (e.g., those containing more than 20 carbon atoms), cracking may be performed to increase the value and/or utility of a stream from an initial distillation. However, such cracking operations are typically very energy intensive since high temperatures (e.g., 500° C.) are generally required to effect the breakdown of higher molecular weight hydrocarbons into lower molecular weight components. Furthermore, the output from such cracking operations is also a complex mixture, and accordingly, may require additional separation (e.g., distillation) to separate the output stream into useful and/or desired fractions having target specifications, e.g., based on boiling point range or chemical composition.

Accordingly, the various components streams produced from petroleum refining and/or processing are generally mixtures. The homogeneity or heterogeneity of those mixtures may be a factor of the character of the crude feedstock, the conditions at which separations are conducted, the characteristics of a cracked stream, and the specifications of an end user for purity of a product stream. However, in practical terms, higher purity streams will require more rigorous separation conditions to isolate a desired compound from related compounds with similar boiling points (e.g., compounds having boiling points within 20, 10, or 5° C. of each other). Such rigorous separations generally require large process units (e.g., larger distillation columns) to separate more closely related compounds (e.g., compounds which have relatively close boiling points).

Furthermore, in addition to the above-described environmental concerns and energy/infrastructure costs associated with petroleum production and refining, there is mounting concern that the use of petroleum as a basic raw material in the production of chemical feedstocks and fuels contributes to environmental degradation (e.g., global warming) via generation and/or release of oxides of carbon. For example, burning a gallon of typical gasoline produces over 19 pounds of carbon dioxide. Because no carbon dioxide is consumed by a refinery in the manufacture of gasoline, the net carbon dioxide produced from burning a gallon of petroleum-derived gasoline is at least as great as the amount of carbon contained in the fuel, and is typically higher when the combustion of additional petroleum required to power the refinery (e.g., for separation of petroleum to produce the gasoline) and to power the transportation vehicles, pumps along pipelines, ships, etc. that bring the fuel to market is considered. Likewise, the production of basic chemicals (e.g., ethylene, propylene, butenes, butadiene, and aromatics such as benzene, toluene, and xylenes) from petroleum does not consume carbon dioxide, and the energy required to power the refinery to produce such chemicals and the transportation vehicles to deliver those chemicals also generate carbon dioxide.

In contrast to fossil fuels and petroleum derived chemicals, the net carbon dioxide produced by burning a gallon of biofuel or biofuel blend, or by producing biomass derived chemicals is less than the net carbon dioxide produced by burning a gallon of petroleum derived fuel or in producing chemicals from petroleum. In addition, biomass-derived chemical and fuel production has far fewer environmental hazards associated with it, since production of biomass-derived fuels requires no drilling operations. Further, biomass-derived chemical and fuel facilities can be located in a wide range of locations relative to petroleum refineries, essentially almost anywhere appropriate feedstocks are available (e.g., where sufficient amounts of suitable plant matter are available). Thus, the requirement for transport of feedstock can minimized, as are the associated energy costs of such transport. Further, even if transport of raw materials is needed, the environmental hazards of a spill of a typical biomass feedstock (e.g., corn) are negligible. Furthermore, biomass-derived product streams are typically far less complex mixtures than product streams from petroleum refining operations. Thus, far less energy may be required to obtain high purity product streams from biomass-based chemical production operations.

However, most biofuels and biomass-derived organic chemicals are produced from relatively expensive feedstocks (compared to petroleum), or are produced by processes which may be relatively inflexible or cannot readily adapt to changes in raw material costs or product prices. As a result, many biomass-based processes have difficulty competing economically with petroleum-based (e.g. refinery) processes.

SUMMARY OF THE INVENTION

The present invention is directed to an integrated process for producing a mixture of renewable biofuels and/or biofuel precursors, as well as a variety of different renewable chemicals from renewable ethanol and renewable isobutanol.

In various embodiments, the present invention is directed to an integrated process for preparing renewable hydrocarbons from renewable isobutanol and renewable ethanol, comprising dehydrating the renewable isobutanol, thereby forming a renewable butene mixture comprising one or more renewable linear butenes and renewable isobutene; dehydrating the renewable ethanol, thereby forming renewable ethylene; and reacting at least a portion of the renewable butene mixture and at least a portion of the renewable ethylene to form one or more renewable C_5-C_{15} olefins.

In other embodiments, the integrated process further comprises forming renewable hydrogen by one or more of: (i) dehydrogenating at least a portion of linear butenes formed by dehydrating renewable isobutanol and/or one or more renewable C_2-C_{15} olefins isolated from renewable C_5-C_{15} olefins formed from reacting at least a portion of a renewable butene mixture and at least a portion of a renewable ethylene stream, thereby forming one or more renewable C_4-C_6 dienes and renewable hydrogen; (ii) dehydrocyclizing at least a portion of one or more renewable C_6-C_{16} olefins isolated from the renewable C_5-C_{15} olefins formed from reacting at least a portion of a renewable butene mixture and at least a portion of a renewable ethylene stream, thereby forming one or more renewable C_6-C_{16} aromatics and renewable hydrogen; (iii) dehydrocyclizing at least a portion of one or more renewable C_6-C_{16} dienes isolated from the renewable C_4-C_6 dienes formed by dehydrogenating at least a portion of linear butenes formed by dehydrating renewable isobutanol and/or one or more renewable C_2-C_{16} olefins isolated from renewable C_5-C_{16} olefins formed from reacting at least a portion of a renewable butene mixture and at least a portion of a renewable ethylene stream, to form one or more renewable C_6-C_{16} aromatics and renewable hydrogen. The integrated process may also comprise hydrogenating at least a portion of the

renewable C_3-C_{16} olefin stream with renewable hydrogen, thereby forming a renewable saturated hydrocarbon fuel or fuel additive.

In still other embodiments, the process of the present invention further comprises controlling the total amount of renewable hydrogen produced by said dehydrogenating and/or dehydrocyclizing, so that the total amount of renewable hydrogen produced is consumed by hydrogenating the renewable C_3-C_{16} olefins.

In other embodiments, the process of the present invention further comprises forming the one or more renewable C_3-C_{16} olefins by disproportionation, metathesis, oligomerization, isomerization, alkylation, and combinations thereof.

The present integrated processes provide a flexible, environmentally sound method or system for producing biomass-derived chemicals, fuels and/or fuel blends. The present integrated process may provide product streams which can be readily and flexibly adapt to different biomass feedstocks, and may produce different mixtures of renewable products based on market demand. The present integrated process may also advantageously provide product streams having well-defined, predictable chemical compositions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic diagram of the formation of butene isomers from the dehydration of isobutanol.

FIG. **2** is a schematic of a unit operation for dehydrating isobutanol to isobutene (isobutylene).

FIG. **3** is a plot of butene isomer equilibrium composition as a function of dehydration temperature.

FIG. **4** is a schematic of a method of preparing C_5 dienes (e.g., isoprene) from C_4 olefins (e.g., isobutene) by the Prins reaction.

FIG. **5** is a schematic of the dehydrogenation of n-butane.

FIG. **6** is a schematic of the dehydrogenation of 1-butene to 1,3-butadiene.

FIG. **7** is a schematic of the acid-catalyzed rearrangement of isobutene

FIG. **8** is a schematic of the formation of benzene, acetone, propylene oxide, phenol, and bisphenol A from renewable propylene.

FIG. **9** is a schematic of the formation of butyraldehyde, isobutyraldehyde, n-butanol, isobutanol, 2-ethylhexanol, and 2-ethylhexanoic acid from propylene and ethylene.

FIG. **10** is a schematic of an integrated process for converting renewable isobutanol to renewable p-xylene.

DETAILED DESCRIPTION OF THE INVENTION

All documents cited herein are incorporated by reference in their entirety for all purposes to the same extent as if each individual document was specifically and individually indicated to be incorporated by reference.

DEFINITIONS

"Renewably-based" or "renewable" denote that the carbon content of the renewable alcohol (and olefin, di-olefin, etc., or subsequent products prepared from renewable alcohols, olefins, di-olefins, etc. as described herein), is from a "new carbon" source as measured by ASTM test method D 6866-05, "Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis", incorporated herein by reference in its entirety. This test method measures the $^{14}C/^{12}C$ isotope ratio in a sample and compares it to the $^{14}C/^{12}C$ isotope ratio in a standard 100% biobased material to give percent biobased content of the sample. "Biobased materials" are organic materials in which the carbon comes from recently (on a human time scale) fixated CO_2 present in the atmosphere using sunlight energy (photosynthesis). On land, this CO_2 is captured or fixated by plant life (e.g., agricultural crops or forestry materials). In the oceans, the CO_2 is captured or fixated by photosynthesizing bacteria or phytoplankton. For example, a biobased material has a $^{14}C/^{12}C$ isotope ratio greater than 0. Contrarily, a fossil-based material has a $^{14}C/^{12}C$ isotope ratio of about 0. The term "renewable" with regard to compounds such as alcohols or hydrocarbons (olefins, di-olefins, polymers, etc.) also refers to compounds prepared from biomass using thermochemical methods (e.g., Fischer-Tropsch catalysts), biocatalysts (e.g., fermentation), or other processes, for example as described herein.

A small amount of the carbon atoms of the carbon dioxide in the atmosphere is the radioactive isotope ^{14}C. This ^{14}C carbon dioxide is created when atmospheric nitrogen is struck by a cosmic ray generated neutron, causing the nitrogen to lose a proton and form carbon of atomic mass 14 (^{14}C), which is then immediately oxidized to carbon dioxide. A small but measurable fraction of atmospheric carbon is present in the form of $^{14}CO_2$. Atmospheric carbon dioxide is processed by green plants to make organic molecules during the process known as photosynthesis. Virtually all forms of life on Earth depend on this green plant production of organic molecules to produce the chemical energy that facilitates growth and reproduction. Therefore, the ^{14}C that forms in the atmosphere eventually becomes part of all life forms and their biological products, enriching biomass and organisms which feed on biomass with ^{14}C. In contrast, carbon from fossil fuels does not have the signature $^{14}C/^{12}C$ ratio of renewable organic molecules derived from atmospheric carbon dioxide. Furthermore, renewable organic molecules that biodegrade to CO_2 do not contribute to global warming as there is no net increase of carbon emitted to the atmosphere.

Assessment of the renewably based carbon content of a material can be performed through standard test methods, e.g., using radiocarbon and isotope ratio mass spectrometry analysis. ASTM International (formally known as the American Society for Testing and Materials) has established a standard method for assessing the biobased content of materials. The ASTM method is designated ASTM-D6866.

The application of ASTM-D6866 to derive "biobased content" is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of radiocarbon (^{14}C) in an unknown sample compared to that of a modern reference standard. This ratio is reported as a percentage with the units "pMC" (percent modern carbon). If the material being analyzed is a mixture of present day radiocarbon and fossil carbon (containing very low levels of radiocarbon), then the pMC value obtained correlates directly to the amount of biomass material present in the sample.

Throughout the present specification, reference to alcohols, olefins, di-olefins, etc., and higher molecular weight materials (e.g., isooctene/isooctane, polymers, copolymers, etc.) made from such compounds is synonymous with "renewable" alcohols, "renewable" olefins, "renewable" di-olefins, etc., and "renewable" materials (e.g., "renewable" isooctene/isooctane, "renewable" polymers, "renewable" copolymers, etc.) unless otherwise indicated. Unless otherwise specified, all such chemicals produced by the integrated processes described herein are renewable unless explicitly stated otherwise.

Throughout the present specification, the terms "olefin" and "alkene" are used interchangeably to refer to a hydrocarbon having at least one carbon-carbon double bond. Alkenes or olefins having two carbon-carbon double bonds can be referred to as dienes, and if the two carbon-carbon double bonds are adjacent in the molecule (e.g., four adjacent sp^2 carbon atoms), the molecule can be termed a conjugated diene.

The renewable alcohols, olefins, di-olefins, polymers, aliphatic and aromatic organic compounds, etc. of the present invention have pMC values of at least about 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, inclusive of all values and subranges therebetween.

Throughout the present specification, the term "about" may be used in conjunction with numerical values and/or ranges. The term "about" is understood to mean those values near to a recited value. For example, "about 40 [units]" may mean within ±25% of 40 (e.g., from 30 to 50), within ±20%, ±15%, ±10%, ±9%, ±8%, ±7%, ±6%, ±5%, ±4%, ±3%, ±2%, ±1%, less than ±1%, or any other value or range of values therein or therebelow. Furthermore, the phrases "less than about [a value]" or "greater than about [a value]" should be understood in view of the definition of the term "about" provided herein.

Throughout the present specification, numerical ranges are provided for certain quantities. It is to be understood that these ranges comprise all subranges therein. Thus, the range "from 50 to 80" includes all possible ranges therein (e.g., 51-79, 52-78, 53-77, 54-76, 55-75, 60-70, etc). Furthermore, all values within a given range may be an endpoint for the range encompassed thereby (e.g., the range 50-80 includes the ranges with endpoints such as 55-80, 50-75, etc.).

Throughout the present specification, the words "a" or "an" are understood to mean "one or more" unless explicitly stated otherwise. Further, the words "a" or "an" and the phrase "one or more" may be used interchangeably.

Overall Process

In various embodiments, the present invention is directed to an integrated process for preparing various renewable hydrocarbons from renewable ethanol and renewable isobutanol. The renewable ethanol and isobutanol can be sold as commodity chemicals directly, or dehydrated to their respective olefins (e.g. ethylene and isobutene and one or more renewable linear butenes—typically a mixture of isobutene, 1-butene and cis/trans-2-butene). The renewable ethylene and renewable butenes can then also either be sold directly, or further processed (e.g., separated or reacted) in a variety of different ways to produce a wide variety of renewable hydrocarbon product streams. In certain embodiments, further processing may comprise mixing the renewable ethylene and/or butenes with ethylene and/or butylene produced by conventional methods (e.g., petroleum cracking) to produce an array of hydrocarbon compounds comprising renewable carbon. Accordingly, such compounds, while not composed solely of renewable carbon, still comprise at least some renewable carbon, with concomitant environmental advantages as described herein.

For example, one renewable hydrocarbon product stream is renewable ethylene, produced from dehydration of renewable ethanol. The renewable ethylene produced thereby is generally of very high purity, and is easily separated from the unreacted feedstock of the dehydration reaction (typically aqueous ethanol and catalyst) by removal of the produced ethylene from the reaction space as a gas stream. The renewable ethylene can then be either sold directly as a feedstock, or subsequently converted to higher value renewable hydrocarbons, such as higher molecular weight olefins produced by oligomerization reactions (e.g. dimers, trimers, etc.), polymerized to form renewable polyethylene, oxidized form renewable ethylene oxide (which can be subsequently be polymerized to form renewable polyethylene oxide, or converted to other renewable polyethylene oxide derivatives), converted to dichloroethane (for subsequent conversion to vinyl chloride and polymerization thereof), used as a renewable feedstock for alkylating other olefins or aromatics (e.g., alkylation of benzene to produce ethylbenzene), etc.

Another renewable hydrocarbon product stream is renewable butene, produced from the dehydration of renewable isobutanol. The renewable butene formed thereby is typically a tunable mixture of butene isomers, which is easily separated from the isobutanol feed to the dehydration reaction, and can be sold directly as a mixture, reacted as a mixture to form other hydrocarbons (e.g., polybutenes), or the mixture of renewable butene isomers can be separated (e.g., by distillation, by selective conversion, etc.) into individual butene isomers, which can then either be sold individually as feedstocks, polymerized (e.g. to renewable polyisobutylene or butene copolymers), oligomerized (e.g., dimerized, trimerized, etc.) to form higher molecular weight olefins (e.g. isooctene or pentamethylheptenes), isomerized (e.g. isobutene isomerized to linear butenes, 1-butene isomerized to 2-butene, or 2-butene isomerized to 1-butene, etc.), dehydrogenated (e.g. to butadiene), as well as combinations of such processes, etc. In particular, isobutene dimers and trimers can be hydrogenated to provide, e.g., renewable isooctane and renewable pentamethylheptenes, both of which are useful as, e.g., renewable transportation fuels or renewable additives for transportation fuels.

In addition, the renewable olefins provided by the integrated processes described herein can also be reacted together, e.g., disproportionated, to provide olefins of varying carbon number (e.g., 3, 5, 7, etc.). For example, renewable ethylene and renewable 2-butene produced as described herein can be disproportionated using appropriate conditions (e.g., an appropriate metathesis catalyst) to provide renewable propylene. Renewable propylene produced by such a disproportionation process can be sold directly as a feedstock, or subsequently converted to other higher value renewable hydrocarbons by, e.g., oligomerization to produce higher olefins (e.g. dimers, trimers, etc.), polymerization to form polypropylene, oxidation to form propylene oxide (which can be subsequently be polymerized to form renewable polypropylene oxide, or converted to other renewable polypropylene oxide derivatives), oxidation to form acrylic acid (which may be further reacted to form a range of commercially significant acrylic esters), reaction with ammonia and oxygen to form acrylonitrile, reaction with benzene to produce acetone and phenol (e.g., via the cumene process), etc.

Similarly, disproportionation and/or oligomerization reactions of ethylene, butenes, propylene and oligomers thereof can be combined in various ways to produce a range of olefins having a desired number of carbon atoms. The various monoolefins produced by such reactions can be dehydrogenated to form dienes or other polyenes (trienes, etc.) and renewable hydrogen as a valuable co-product. In addition, olefins and/or polyenes produced by these reactions can also be dehydrocyclized to form cyclic olefins (e.g., cyclohexene) or aromatics (e.g., benzene, xylenes), which also produces renewable hydrogen. Furthermore, the reactivity of olefins is suited to selective introduction of heteroatoms into the above-described olefins (e.g., oxygen, nitrogen, halogens, etc.), allowing access to a broad array of derivatives.

Thus, beginning with simple, renewable ethanol and isobutanol feedstocks, the integrated process of the present inven-

tion can provide essentially all of the commercially important hydrocarbons currently produced in petrochemical refineries (e.g., ethylene, propylene, butenes, butadiene, xylenes such as p-xylene, toluene, and benzene), and when coupled with additional processes, can produce virtually any fuel or chemical. In particular, the present invention provides a method for the production of benzene and xylene, commodity chemicals which serve as the building blocks from a vast array of intermediates and finished products. Furthermore, when the ethanol and isobutanol feedstocks are renewable, produced from biomass or other biological sources, the integrated process of the present invention can produce renewable hydrocarbons corresponding to the petroleum-derived hydrocarbons produced in a conventional petroleum refinery in a more environmentally sound and sustainable fashion. Further still, even in cases where the use of solely renewable feedstocks is not feasible and/or economical, supplementing traditional petroleum-derived hydrocarbon feedstocks (e.g., ethylene, butenes, etc.) with renewable feedstocks in integrated chemical processing and/or manufacturing operations can still provide substantive advantages (e.g., reduced environmental impact, carbon footprint, etc.) relative to traditional, "petroleum-only" operations.

In contrast to the present methods, petroleum-derived ethylene, butenes and/or propylene are typically produced in catalytic cracking of higher molecular weight hydrocarbons, as component in a complex mixture of hydrocarbons. Such mixtures typically include, among a range of product compounds, low molecular weight olefins such as propylene, butene, and butadiene, which may be difficult to separate due to their similar boiling points. Accordingly, purifying such a stream to produce a high-purity ethylene, propylene, butenes, or butadiene fractions is typically an energy intensive process. In fact, mixtures of ethylene, propylene, butene and butadiene are often sold directly as liquefied mixtures by refineries, as a commodity, rather than separating the individual fractions, due to the costs of equipment and energy required to separate the various components of such mixtures. However, if desired, the present integrated processes can provide such a mixture analogous to that provided by refinery cracking processes, thus supplying a typical refinery product for end users who rely on such mixed feedstocks. Furthermore, mixtures of hydrocarbons produced by the present methods typically have a well-defined composition due to the limited number of possible products associated with each individual process or reactive step. Accordingly, the present integrated methods may provide higher purity products requiring less additional processing and/or energy to separate. Alternatively, the present integrated process may provide mixed streams with simpler, well-defined compositions.

The relative amounts of product outputs produced in the processes described herein can be flexibly adjusted in various ways to adjust to, e.g., changing market demand for specific product streams or to maximize the overall value of the products produced. For example, the relative amounts of ethanol and isobutanol supplied to the process of the present invention can be adjusted, or the relative amounts of, e.g., ethylene and isobutene (and/or linear butenes, etc.) supplied to various unit operations can be adjusted to vary the product mix, and thereby maximize the economic value of the products produced. Since the catalysts described herein for producing renewable ethanol and renewable isobutanol use similar biomass raw material, the relative output from a given unit input of biomass can be adjusted as desired to a higher or lower fraction of either ethanol or isobutanol. As a result, varying demand for products produced downstream can be accommodated by adjusting relative production of ethanol and isobutanol (and intermediates and/or products subsequently formed therefrom).

For example, if market demand and/or market price for ethylene (or products formed therefrom) is high, the relative amount of ethanol feedstock can be increased, and accordingly, the amount of ethylene produced via dehydration of ethanol can be increased. Similarly, if market demand and/or market price for butylene(s) (or products formed therefrom) is high, the relative amount of isobutanol feedstock can be increased, and accordingly, the amount of butylene(s) produced via dehydration of isobutanol can be increased. In another case, if market demand and/or market price for propylene (or products prepared from propylene) increases, the relative amounts of renewable ethanol and isobutanol fed into the process can be adjusted to optimize the relative amounts of ethylene and 2-butene feedstocks for subsequent disproportionation to propylene. Similarly, in situations where fuel prices are high and/or fuel demand is high, the amount of isobutanol relative to ethanol fed into the process of the present invention can be increased to maximize production of isooctene and/or pentamethylheptenes (dimer and trimer of isobutylene), and optionally the relative amount of olefins fed to dehydrocyclization could be increased in order to supply the necessary hydrogen to reduce the isooctene and/or pentamethylheptenes to the respective isooctane and pentamethylheptanes.

Alternatively, if it is desirable to maximize the production of aromatics and dienes such as butadiene, the process can be adjusted to maximize production of butadiene and aromatics such as benzene and xylenes (and/or products downstream such as styrene, cumene, etc.), and the excess hydrogen produced from dehydrogenation of linear butenes to butadiene or aromatic-forming cyclodehydrogenations can be sold or utilized to hydrogenate isooctene and/or pentamethylheptenes to isooctane (e.g., for gasoline) and/or pentamethylheptanes (e.g., for jet fuel). Thus, the amount and composition of feedstocks fed to the present integrated process, and the relative quantities of produced product in the various unit operations described herein can be increased or decreased to maximize the overall value of the products produced while ensuring complete utilization of the renewable carbon and optionally hydrogen produced in the integrated process.

In certain embodiments, the process of the present invention utilizes most or all of all the carbon in the ethanol and isobutanol feedstock, and most or all of the renewable hydrogen produced by dehydrogenation and/or dehydrocyclization reactions, to form a renewable saturated hydrocarbon fuel or fuel active product stream and one or more additional high-value product streams. Within the constraint of complete utilization of carbon and hydrogen produced in the process, the amount of saturated hydrocarbon fuel or fuel additive and the selection and amount of other high-value product streams can be adjusted to meet variations in market demand and market value for different product streams.

Production of Alcohols

The processes of the present invention for making renewable compositions, as described herein, typically begin with the formation of renewable alcohols (e.g., renewable ethanol and renewable isobutanol), e.g., from biomass. The term "formation from biomass" includes any combination of methods including fermentation, thermochemical (e.g., Fischer-Tropsch), photosynthesis, etc. Renewable alcohol (e.g., ethanol and isobutanol) streams can be prepared from biomass, by the same method, or by different methods, or portions of the ethanol and/or isobutanol can be prepared by a combination of different methods. A range of renewable alcohols, e.g.,

ethanol, 1-butanol, 2-butanol, isobutanol, tert-butanol, pentanols, etc. (and the corresponding renewable olefins or other chemicals) may be produced and employed in the integrated processes described herein.

When renewable ethanol and renewable isobutanol are formed by fermentation, the feedstock for the fermentation process can be any suitable fermentable feedstock known in the art, for example sugars derived from agricultural crops such as sugarcane, corn, etc. Alternatively, the fermentable feedstock can be prepared by the hydrolysis of biomass, for example lignocellulosic biomass (e.g. wood, corn stover, switchgrass, herbiage plants, ocean biomass, etc.). The lignocellulosic biomass can be converted to fermentable sugars by various processes known in the art, for example acid hydrolysis, alkaline hydrolysis, enzymatic hydrolysis, or combinations thereof. In such processes, the carbohydrate component of the biomass (e.g. cellulose and hemicellulose) are broken down by hydrolysis to their constituent sugars, which can then be fermented by suitable microorganisms as described herein to provide ethanol or isobutanol.

Typically, woody plants comprise about 40-50% cellulose, 20-30% hemicellulose, and 20-28% lignin, with minor amounts of minerals and other organic extractives. The cellulose component is a polysaccharide comprising glucose monomers coupled with β-1,4-glycoside linkages. The hemicellulose component is also a polysaccharide, but comprising various five-carbon sugars (usually xylose and arabinose), six-carbon sugars (galactose, glucose, and mannose), and 4-O-methyl glucuronic acid and galacturonic acid residues. The cellulose and hemicellulose components are hydrolyzed to fermentable five- and six-carbon sugars which can then be used as a feedstock for the fermentation as described herein. Residual carbon compounds, lignin (a highly branched polyphenolic substance), and organic extractives (e.g., waxes, oils, alkaloids, proteins, resins, terpenes, etc.) can be separated from the sugars at various stages of the hydrolysis process and utilized in various ways, for example, burned has a fuel to provide energy/heat for the fermentation process and/or for subsequent processes (e.g., dehydration, oligomerization, dehydrogenation, etc.).

In one embodiment, the ethanol and isobutanol are both formed by one or more fermentation steps as described herein. Any suitable microorganism can be used to prepare renewable ethanol and butanols. Ethanol can be produced by microorganisms known in the art such as *Saccharomyces cerevisiae*. Butanols can be produced, for example, by the microorganisms described in U.S. Patent Publication Nos. 2007/0092957, 2008/0138870, 2008/0182308, 2007/0259410, 2007/0292927, 2007/0259411, 2008/0124774, 2008/0261230, 2009/0226991, 2009/0226990, 2009/0171129, 2009/0215137, 2009/0155869, 2009/0155869, 2008/02745425, etc. Additionally, butanols and other higher alcohols are produced by yeasts during the fermentation of sugars into ethanol. These fusel alcohols are known in the art of industrial fermentations for the production of beer and wine and have been studied extensively for their effect on the taste and stability of these products. Recently, production of fusel alcohols using engineered microorganisms has been reported (U.S. Patent Application No. 2007/0092957, and *Nature* 2008 (451) 86-89).

Renewable ethanol and renewable isobutanol prepared by fermentation are, in most embodiments, produced in fermentors and/or under conditions optimal for fermentation of the respective alcohol. That is, renewable ethanol is produced in one or more fermentors optimized for production of ethanol and operated under conditions optimized for the production of ethanol (e.g., using microorganisms which produce high yields of ethanol, a fermentable feedstock with suitable nutrients optimal for ethanol-producing microorganisms, temperature conditions and ethanol recovery unit operations optimized for ethanol production, etc.). Likewise, renewable isobutanol is produced in one or more fermentors under conditions optimized for the production of isobutanol (e.g., using microorganisms which produce high yields of isobutanol, a fermentable feedstock with suitable nutrients optimal for isobutanol-producing microorganisms, temperature conditions and isobutanol recovery unit operations optimized for isobutanol production, etc.). In particular embodiments, ethanol is produced in a conventional ethanol fermentation plant and isobutanol is produced in an ethanol fermentation plant retrofitted for the production of isobutanol, for example as described in US 2009/0171129.

In one embodiment, the retrofitted ethanol plant includes an optional pretreatment unit, multiple fermentation units, and a beer still to produce isobutanol. The isobutanol is produced by optionally pretreating a feedstock (e.g., ground corn) to form fermentable sugars in the pretreatment unit. A suitable microorganism, as described herein, is cultured in a fermentation medium comprising the fermentable sugars in one or more of the fermentation units to produce isobutanol. The isobutanol can be recovered from the fermentation medium as described herein, and as described in US 2009/0171129.

Renewable ethanol and butanols can also be prepared using various other methods such as conversion of biomass by thermochemical methods, for example by gasification of biomass to synthesis gas followed by catalytic conversion of the synthesis gas to alcohols in the presence of a catalyst containing elements such as copper, aluminum, chromium, manganese, iron, cobalt, or other metals and alkali metals such as lithium, sodium, and/or potassium (*Energy and Fuels* 2008 (22) 814-839). The various alcohols, including ethanol and butanols can be separated from the mixture by distillation and used to prepare renewable ethylene or renewable butenes, or compounds derived from renewable ethylene and/or butenes as described herein. Alcohols other than ethanol and isobutanol can be recovered and utilized as feedstocks for other processes, burned as fuel or used as a fuel additive, etc.

Alternatively, renewable ethanol and butanols can be prepared photosynthetically, e.g., using cyanobacteria or algae engineered to produce isobutanol, isopentanol, and/or other alcohols (e.g., *Synechococcus elongatus* PCC7942 and *Synechocystis* PCC6803; see Angermayr et al., *Energy Biotechnology with Cyanobacteria. Curr Opin Biotech* 2009 (20) 257-263; Atsumi and Liao, *Nature Biotechnology* 2009 (27) 1177-1182; and Dexter et al., *Energy Environ. Sci.* 2009 (2), 857-864, and references cited in each of these references). When produced photosynthetically, the "feedstock" for producing the resulting renewable alcohols is light, water and CO_2 provided to the photosynthetic organism (e.g., cyanobacteria or algae).

Higher alcohols other than butanols or pentanols produced during fermentation (or other processes as described herein for preparing renewable ethanol and butanols) may be removed from the ethanol or butanol prior to carrying out subsequent unit operations (e.g., dehydration). The separation of these higher alcohols from the butanol(s) (e.g. isobutanol) or pentanol(s) (e.g. 1-pentanol, 2-pentanol, 3-pentanol, branched or cyclic pentanols, etc.) can be effected using known methods such as distillation, extraction, etc. Alternatively, these higher alcohols can remain mixed in the butanol(s) or pentanol(s), and can be removed after subsequent processing. For example, any higher alcohols mixed in with isobutanol can be dehydrated with the isobutanol stream

to the corresponding olefins, then separated from the mixed butenes. The determination of whether to remove such higher alcohols prior to dehydration, or to remove the corresponding olefin after dehydration (or the corresponding dehydrogenation byproducts/co-products) generally depends on the relative ease and cost of the respective separations and the relative value of the byproducts/co-products. In some cases, the amounts of such by-products may be low enough that removal is uneconomic and a product olefin stream may be used directly with such minor impurities if a subsequent product is tolerant to such impurities. For example, subsequent the polymerization of a product mixed butene stream (and the specification of a product polymer produced thereby) may be such that minor amounts of, e.g., pentenes or other olefins, may be acceptable, and separation of those minor components may be unnecessary. Alternatively, in certain cases, higher alcohols such as pentanols (e.g., 1-pentanol, 2-pentanol, 3-pentanol, branched or cyclic pentanols, etc.) may be produced in sufficient quantities for use in the present integrated processes. For example, higher alcohols, e.g., linear pentanols in sufficient amounts and subject to subsequent reaction/processing to provide an additional feedstock (e.g., pentenes, pentadienes, etc.) for the present integrated processes. Other higher alcohols may similarly produced, separated, processed, reacted, etc. as desired.

Isolation of Alcohols from Fermentation

When the renewable ethanol and isobutanol are prepared by fermentation, the ethanol can be removed from the fermentor by methods known in the art, for example steam stripping, distillation, pervaporation, etc. (see, e.g., Perry & Chilton, Chemical Engineers Handbook, 4th Ed.).

Isobutanol can also be removed from the fermentor by various methods, for example fractional distillation, solvent extraction (e.g., with a renewable solvent such as renewable oligomerized hydrocarbons, renewable hydrogenated hydrocarbons, renewable aromatic hydrocarbons, etc. prepared as described herein), gas stripping, adsorption, pervaporation, etc., or by combinations of such methods, prior to dehydration. In certain embodiments, ethanol and butanol are removed from the fermentor in the vapor phase under reduced pressure (e.g., as an azeotrope with water as described in U.S. Pat. Appl. Pub. No. 2009/0171129). In some such embodiments, the fermentor itself is operated under reduced pressure without the application of additional heat (other than that used to provide optimal fermentation conditions for the microorganism) and without the use of distillation equipment, and the produced isobutanol is removed as an aqueous vapor (or azeotrope) from the fermentor. In other such embodiments, the fermentor is operated under approximately atmospheric pressure or slightly elevated pressure (e.g., due to the evolution of gases such as CO_2 during fermentation) and a portion of the feedstock containing the isobutanol is continuously recycled through a flash tank operated under reduced pressure, whereby the isobutanol is removed from the headspace of the flash tank as an aqueous vapor or water azeotrope. These latter embodiments have the advantage of providing for separation of the isobutanol without the use of energy intensive or equipment intensive unit operations (e.g., distillation), as well as continuously removing a metabolic by-product of the fermentation, thereby improving the productivity of the fermentation process. The resulting wet isobutanol can be dried and then dehydrated, or dehydrated wet (as described herein), then subsequently dried.

The production of renewable isobutanol by fermentation of carbohydrates typically co-produces small (<5% w/w) amounts of 3-methyl-1-butanol and 2-methyl-1-butanol and much lower levels of other fusel alcohols. One mechanism by which these by-products form is the use of intermediates in hydrophobic amino acid biosynthesis by the isobutanol-producing metabolic pathway that is engineered into the host microorganism. The genes involved with the production of intermediates that are converted to 3-methyl-1-butanol and 2-methyl-1-butanol are known and can be manipulated to control the amount of 3-methyl-1-butanol produced in these fermentations (see, e.g., Connor and Liao, *Appl Environ Microbiol* 2008 (74) 5769). Removal of these genes can decrease 3-methyl-1-butanol and/or 2-methyl-1-butanol production to negligible amounts, while overexpression of these genes can be tuned to produce any amount of 3-methyl-1-butanol in a typical fermentation. Alternatively, the thermochemical conversion of biomass to mixed alcohols produces both isobutanol and these pentanols. Accordingly, when biomass is converted thermochemically, the relative amounts of these alcohols can be adjusted using specific catalysts and/or reaction conditions (e.g., temperature, pressure, etc.).

Dehydration to Ethylene and Butenes

Renewable ethanol and butanols obtained by biochemical or thermochemical production routes as described herein can be converted into their corresponding olefins by reacting the alcohols over a dehydration catalyst under appropriate conditions (see e.g. FIG. **1**). Typical dehydration catalysts that convert alcohols such as ethanol and isobutanol into ethylene and butene(s) include various acid treated and untreated alumina (e.g., γ-alumina) and silica catalysts and clays including zeolites (e.g., β-type zeolites, ZSM-5 or Y-type zeolites, fluoride-treated β-zeolite catalysts, fluoride-treated clay catalysts, etc.), sulfonic acid resins (e.g., sulfonated styrenic resins such as Amberlyst® 15), strong acids such as phosphoric acid and sulfuric acid, Lewis acids such boron trifluoride and aluminum trichloride, and many different types of metal salts including metal oxides (e.g., zirconium oxide or titanium dioxide) and metal chlorides (e.g., Latshaw BE, Dehydration of Isobutanol to Isobutylene in a Slurry Reactor, Department of Energy Topical Report, February 1994).

Dehydration reactions can be carried out in both gas and liquid phases with both heterogeneous and homogeneous catalyst systems in many different reactor configurations (see, e.g., FIG. **2**). Typically, the catalysts used are stable to the water that is generated by the reaction. The water is usually removed from the reaction zone with the product. The resulting alkene(s) either exit the reactor in the gas or liquid phase, depending upon the reactor conditions, and may separated and/or purified downstream or further converted in the reactor to other compounds (e.g., isomers, dimers, trimers, etc.) as described herein. The water generated by the dehydration reaction may exit the reactor with unreacted alcohol and alkene product(s) and may be separated by distillation or phase separation. Because water is generated in large quantities in the dehydration step, the dehydration catalysts used are generally tolerant to water and a process for removing the water from substrate and product may be part of any process that contains a dehydration step. For this reason, it is possible to use wet (e.g., up to about 95% or 98% water by weight) alcohol as a substrate for a dehydration reaction, then remove water introduced with alcohol in the reactor feed stream with the water generated by the dehydration reaction during or after the dehydration reaction (e.g., using a zeolite catalyst such as those described U.S. Pat. Nos. 4,698,452 and 4,873,392). Additionally, neutral alumina and zeolites can dehydrate alcohols to alkenes but generally at higher temperatures and pressures than the acidic versions of these catalysts. In certain embodiments, the alkene(s) produced in the dehydration reaction are isolated after the dehydration step, before being used as feedstocks for subsequent process steps (e.g.,

oligomerization, dehydrogenation, disproportionation, etc.). Depending on the particular configuration of the process, isolation of the alkenes after formation in the dehydration reactor can offer certain advantages, for example when the dehydration is carried out in the gas phase, while subsequent process steps are carried out in the liquid phase. However, in certain other embodiments of the process of the present invention, the alkenes can be used directly from the product stream of the dehydration reactor, without isolation (e.g., when the dehydration and the subsequent process steps are carried out under similar temperature and pressure conditions and/or when such subsequent steps are relatively insensitive to water).

Renewable ethylene may be produced directly by the dehydration of renewable ethanol. However, when 1-butanol, 2-butanol, or isobutanol are dehydrated, a mixture of four C_4 olefins 1-butene, cis-2-butene, trans-2-butene, and isobutene can be formed. The exact concentration in a product stream of each butene isomer is determined by the thermodynamics of formation of each isomer. Accordingly, the reaction conditions and catalysts used can be manipulated to affect the distribution of butene isomers in the product stream. Thus, one can obtain butene mixtures enriched in a particular isomer. However, production of a single butene isomer by dehydration is generally difficult. For example, dehydration of isobutanol at 280° C. over a γ-alumina catalyst can be optimized to produce up to 97% isobutene despite an expected equilibrium concentration of ~57% at that temperature (see FIG. **3**). However, there is currently no known method for cleanly dehydrating isobutanol to 99+% isobutene (Saad L. and Riad M. *J Serbian Chem Soc* 2008 (73) 997).

The dehydration conditions for isobutanol can be varied in the process of the present invention to provide different butene isomer compositions suitable for producing a desired product mixture. For example, if it is desirable to increase the level of propylene produced by the present process (e.g., by disproportionation of ethylene and 2-butene, as described herein), isobutanol dehydration reaction conditions can be adjusted (e.g., reactor temperature, pressure, residence time, catalyst identity, etc.) to increase the relative amounts of 2-butene in the dehydration product stream.

Alternatively, the dehydration reaction can be combined in various ways with an isomerization reaction (using suitable catalysts and conditions as described herein) to effectively achieve a desired butene isomer distribution. For example, if increased amounts of 2-butene are desired, the 1-butene and isobutene isomers can be recycled one or more times at various stages in the process (e.g., after dehydration of isobutanol, and/or after any other unit operations utilizing a feedstock containing 1-butene or isobutene) to an isomerization reaction to produce additional 2-butene, thereby effectively increasing the amount of 2-butene produced.

Propylene by Metathesis

Propylene is conventionally produced by cracking higher hydrocarbons, and as a byproduct in other processes in petroleum refineries. Renewable propylene could be produced by dehydration of renewable propanols such as isopropanol or n-propanol (e.g. derived from renewable acetone provided by so-called "ABE" fermentation processes, or from propanol produced from biomass by thermochemical processes), but such "ABE" processes are generally relatively inefficient, and the resulting renewable propanol is accordingly not cost competitive with petrochemically derived propanol (e.g., produced by hydroformylation of petroleum derived ethylene). However, renewable propylene can be more efficiently produced by the disproportionation of renewable ethylene and renewable 2-butene. As described herein, ethylene can be readily prepared by dehydration of ethanol, and 2-butene can be prepared by the dehydration of isobutanol under suitable conditions, and/or by the isomerization of renewable isobutene or 1-butene produced by the dehydration of isobutanol.

The specific unit operations employed in the preparation of renewable propylene will depend on the nature of the starting materials and desired ultimate products. For example, renewable propylene can be prepared by separately dehydrating ethanol and butanol, followed by disproportionation of at least a portion of the ethylene and butene(s) produced as described herein (e.g., the remaining portion of the ethylene and butene(s) used in other unit operations), or by the dehydration of mixtures of isobutanol and ethanol to a mixture of ethylene and butylenes, at least a portion of which is then disproportionated in the presence of the appropriate metathesis catalyst to provide propylene. Since dehydration of isobutanol typically produces a mixture of butene isomers, and optimal conditions for dehydrating isobutanol and ethanol are typically somewhat different, in various embodiments the dehydration of isobutanol and ethanol are carried out separately (e.g., in separate dehydration reactors, or at different times in the same dehydration reactor). In particular embodiments, the dehydration of isobutanol and ethanol are carried out in one or more separate isobutanol dehydration reactors and one or more separate ethanol dehydration reactors, and the resulting ethylene and 2-butene are then reacted in one or more metathesis reactors in the presence of an appropriate metathesis catalyst.

Depending upon the specific mixture of butenes formed after dehydration of isobutanol, and the value of particular intermediates or products, a portion of the various butenes can be subjected to various additional unit operations. For example, a portion of the unreacted isobutene can be isomerized to linear butenes (1- and 2-butenes) and the linear butenes (particularly 2-butenes) can be recycled back to the disproportionation step, or the isobutene can be converted to, e.g., tert-butyl ethers or ten-butanol by reaction with alcohols or water, oligomerized and hydrogenated to higher alkanes/alkenes suitable for use in fuels (e.g., isooctane/isooctene), dehydrocyclized to aromatics (e.g., xylenes such as o-xylene, p-xylene or m-xylene), etc. The isomerization of isobutene can be carried out in a separate isomerization step (e.g., in a separate isomerization reactor), or can occur in-situ during the disproportionation reaction by appropriate selection of catalyst in the metathesis reactor.

In some embodiments, renewable propylene is prepared using a method similar to that described in U.S. Pat. No. 7,214,841, in which renewable butenes (e.g., a mixture comprising 1-butene, 2-butenes, and/or isobutene) and renewable ethylene, prepared as described herein, are reacted in the presence of a metathesis catalyst. Since isobutene may also react with renewable 1- or 2-butenes in the presence of a metathesis catalyst (producing, e.g., mixed pentenes and hexenes), in various embodiments isobutene is removed from the butene mixture prior to the metathesis step to minimize formation of pentenes and hexenes. However, pentenes and hexenes are easily separated from ethylene and propylene, and can be used as chemical intermediates for further unit operations in the process of the present invention, or as fuel blend stocks, etc. Accordingly, in some embodiments the isobutene is not removed from the metathesis reaction feedstock, and the resulting pentenes and hexenes are subsequently removed and utilized as described herein, while ethylene can be recycled to the metathesis reaction as feedstock (and the propylene can be recovered). Any isobutene remaining in the metathesis product mixture can be removed and

recycled to a separate rearrangement step (e.g., to produce linear butenes) or diverted to other processes (e.g., oligomerization, oxidation, etc. to produce biofuels, acrylates, aromatics, etc.) as described herein.

In various embodiments, renewable propylene is formed by reacting an approximately 1.3:1 molar mixture of renewable ethylene and renewable 2-butene in a metathesis reactor in the presence of a suitable metathesis catalyst as described herein. The approximately 1.3:1 molar mixture of renewable ethylene and renewable 2-butene can be formed by mixing a suitable portion of the renewable ethylene formed by dehydration of renewable ethanol and a portion of the renewable 2-butene isolated from the mixture of butene isomers formed by dehydration of renewable isobutanol. The renewable 2-butene can be obtained by separation from the mixture of butene isomers formed after dehydration of isobutanol, using suitable methods such as fractional distillation, absorption, etc. In other embodiments, the molar ratio of renewable ethylene and renewable 2-butene can be adjusted depending on the composition of the metathesis feedstock stream(s) and/or the metathesis reaction conditions (e.g., temperature, pressure, residence time, etc.) to maximize production of a desired metathesis product (e.g., propylene) or to adjust the composition of the product stream for subsequent unit operations. For example, when the feedstock comprises a mixture of propylene, isobutene, and linear butenes, it may be desirable to increase the molar ratio of 2-butenes in the feedstock to compensate for side-reactions which can reduce the amount of 2-butenes available for reaction with ethylene (e.g., to maximize propylene production). Alternatively, if metathesis conditions (e.g., addition of an isomerization catalyst such as magnesium oxide) are selected which promote isomerization of 1-butenes and/or isobutene to 2-butenes in the metathesis reactor, the feedstock can comprise lower levels of 2-butenes, so that optimal levels of 2-butenes are provided by 2-butene initially present in the feedstock and 2-butenes produced in-situ in the metathesis reaction by isomerization of isobutene and/or 1-butene.

In still other embodiments, the mixed butenes can be oligomerized over an acidic ion exchange resin under conditions which selectively convert isobutene to isooctene (e.g., using the methods of Kamath et al., *Ind Engr Chem Res* 2006 (45) 1575-1582), but leave the linear butenes substantially unreacted, thereby providing a substantially isobutene-free mixture of linear butenes (e.g., containing less than about 10%, 5%, 4%, 3%, 2%, 1% of isobutene, or any other value or range of values therein or therebelow). After separation of isooctene from the mixed linear butenes, the substantially isobutene-free renewable linear butenes can then be combined with renewable ethylene and reacted in the presence of a metathesis catalyst to form renewable propylene.

The disproportionation/metathesis of ethylene and linear butenes (e.g., 1- and/or 2-butene) can be carried out in the presence of one or more suitable metathesis catalysts, optionally including one or more components which may catalyze the rearrangement of isobutene to linear butenes (particularly 2-butenes) as described herein. A non-limiting list of suitable metathesis catalysts include, for example, oxides, hydroxides, or sulfides of metals such as tungsten, molybdenum, rhenium, niobium, tantalum, vanadium, ruthenium, rhodium, iridium, iron, potassium, chromium, and osmium. These metal oxides/hydroxides/sulfides can be supported on a high surface-area (e.g., 10 m^2/g or more) inorganic carrier known in the catalyst art, such as silica, γ-alumina, titania, etc. The metathesis catalyst can also contain a promoter compound to increase catalyst activity and/or specificity, such as lithium, sodium, potassium, cesium, magnesium, calcium, strontium, barium, zinc, yttrium compounds (e.g., elemental forms as well as oxides, hydroxides, nitrates, acetates, etc., as described in Banks R L and Kukes S G, *J Molec Cat* 1985 (28) 117-1311; U.S. Pat. Pub. No. 2008/0312485; and U.S. Pat. Nos. 4,575,575, and 4,754,098), or an inorganic compound containing a promoter, such as hydrotalcite, or in particular embodiments, tungsten oxide on silica and magnesium oxide (e.g., as described in U.S. Pat. No. 7,214,841). In other embodiments, the renewable linear butenes (produced as described herein by the dehydration of renewable isobutanol) are reacted with renewable ethylene in the presence of a catalyst comprising rhenium oxide on alumina.

Suitable metathesis reaction conditions include those described in U.S. Pat. No. 3,261,879; temperatures ranging from about 250° F. to about 550° F., pressures ranging from about 0-1500 psig, WHSV values ranging from about 0.5 to 20 hr^{-1}, a minimum 30% molar excess ethylene (e.g., moles ethylene at least about 1.3 times moles butenes). Alternatively, suitable metathesis conditions include those described in U.S. Pat. Appl. Pub. No. 2008/0312485; a catalyst comprising a mixture of tungsten oxide on silica and hydrotalcite, reaction temperature of about 200° C., and a reaction pressure of about 3.5 MPa.

In most embodiments, the renewable butenes and ethylene in the metathesis feedstock are purified to remove impurities which may "poison" the metathesis catalyst. For example, purification may include removing water; oxygenates such as carbon dioxide, alcohols, aldehydes, acids, etc.; nitrogen or nitrogen-containing compounds; sulfur-containing compounds such as hydrogen sulfide, ethyl sulfide, diethyl sulfide, methyl ethylsulfide; alkynes such as acetylene and methylacetylene; dienes such as butadiene, etc. In some embodiments, purification may include removing isobutene (as described herein). In various embodiments, the levels of such impurities in the metathesis feedstock are maintained below about 10 ppm, in most embodiments less than 1 ppm. Purification can be carried out using conventional methods, for example the methods described in U.S. Pat. Nos. 3,261,875 and 7,214,841, or U.S. Pat. Appl. Pub. No. 2008/0312485, in which the metathesis feedstock is passed over an absorbent bed comprising alumina, zeolites, magnesium and other metal oxides. In most embodiments, a "poisoned" metathesis catalyst can be regenerated in air at about >1000° F. In particular embodiments the metathesis catalyst is periodically regenerated by heating the catalyst in the presence of oxygen (e.g., air) as described herein. For example, the process of the present invention can employ two or more metathesis reactors such that at least one of the metathesis reactors can be regenerated while the other metathesis reactors are in operation, thereby permitting continuous operation of the process.

Isobutene and Linear Butenes

As described herein, the dehydration of isobutanol typically provides a mixture of butene isomers, including isobutene and linear butenes. Depending upon the dehydration conditions used, the mixture of butenes in an isobutanol dehydration product stream can contain varying amounts of isobutene. For example, if the dehydration is carried out at lower temperatures, typically a higher percentage of the butene product stream comprises isobutene (see FIG. **3**). Accordingly, if higher levels of isobutene production are desirable (e.g., for the production of polyisobutylene, butyl rubber, other butene copolymers, xylenes, etc.), the process conditions of the isobutanol dehydration can be adjusted to increase the percentage of isobutene produced in the isobutanol dehydration product stream. The remaining linear butenes can be isomerized (e.g., in a separate isomerization

reactor) to form additional isobutene, which can then be combined with the isobutene produced from dehydration, or diverted to other processes, e.g., oligomerization, dehydrogenation, dehydrocyclization, isomerized to linear butenes for disproportionation with ethylene to form propylene, etc.

Alternatively, if higher levels of linear butenes are desirable (e.g., for disproportionation with ethylene to form propylene, dehydrogenation to form butadiene, etc.), the isobutanol dehydration process conditions can be adjusted to increase the proportion of linear butenes formed (e.g., by increasing the dehydration process temperature), and the isobutene can be separated from the isobutanol dehydration product stream and isomerized (e.g., in a separate isomerization reactor) to form additional linear butenes, which can be combined with the initially formed linear butenes. Alternatively, if the desired product is butadiene, the mixture of linear butenes and isobutene can be dehydrogenated to form a mixture of isobutene and butadiene. Since isobutene is substantially unreactive to dehydrogenation conditions for forming butadiene from linear butenes, the isobutene remains unreacted in the product stream, and can be readily separated from the butadiene. The unreacted isobutene can then be recycled and isomerized to form additional linear butenes, or diverted to other process steps.

Butadiene

Di-olefins (dienes) such as butadiene are conventionally produced in petrochemical refineries by the cracking reactions that generate C_4-containing olefin streams for petrochemical use. If additional di-olefins are required, they can be produced by dehydrogenation of the C_4 mono-olefins. For example, butadiene may be produced by passing raffinate-2 over a dehydrogenation catalyst.

Dehydrogenation catalysts convert saturated carbon-carbon bonds in organic molecules into unsaturated double bonds (see FIG. **4**). Typical dehydrogenation catalysts include mixtures of metal oxides with varying degrees of selectivity towards specific olefins. For example, in certain oxidative dehydrogenations, iron-zinc oxide mixtures favor 1-butene dehydrogenation while cobalt-iron-bismuth-molybdenum oxide mixtures favor 2-butene dehydrogenation (see, e.g., Jung et al., *Catalysis Letters* 2008 (123), 239). Other examples of dehydrogenation catalysts include vanadium- and chrome-containing catalysts (see, e.g., Toledo-Antonio et al., *Applied Catalysis A* 2002 (234) 137), ferrite-type catalysts (see, e.g., Lopez Nieto et al., *J Catalysis* 2000 (189) 147), manganese-oxide doped molecular sieves (see, e.g., Krishnan V V and Suib S L, *J Catalysis* 1999 (184) 305), copper-molybdenum catalysts (see, e.g., Tiwari et al., *J Catalysis* 1989 (120) 278), and bismuth-molybdenum-based catalysts (see, e.g., Batist et al., *J Catalysis* 1966 (5) 55).

Dehydrogenation of an olefin to a di- or polyolefin can occur if the olefin molecule can accommodate one or more additional double bonds. For example, 1-butene can be dehydrogenated to butadiene (see FIG. **5**). Dehydrogenation catalysts are also capable of rearranging olefinic bonds in a molecule to accommodate a second olefin bond, generally when skeletal rearrangement is not required (e.g., rearrangement by one or more hydrogen shifts), but these catalysts typically do not catalyze skeletal rearrangements (e.g., breaking and reforming C—C bonds) under dehydrogenating conditions. For example, 2-butene can be dehydrogenated to butadiene but isobutene is not typically dehydrogenated to butadiene in the same process unless the reaction conditions/catalysts are selected to both promote skeletal rearrangement and dehydrogenation. Alternatively, one or more process units may be employed, wherein a stream comprising isobutene may be subject to isomerization conditions to promote the formation of linear butenes (e.g., as described herein) to effect skeletal rearrangement, then subsequently subject to dehydrogenation conditions to maximize production of butadiene form a mixed butene stream.

Two major types of dehydrogenation reactions are conventionally used to produce olefins from saturated materials (see, e.g., Buyanov R A, *Kinetics and Catalysis* 2001 (42) 64). A first type, endothermic dehydrogenation, typically uses a dehydrogenation catalyst (e.g., chromia-alumina-based, spinel supported platinum-based, phosphate-based, and iron oxide-based catalysts), high heat (typically 480-700° C.), and a reactor configuration (typically fixed-bed and fluidized-bed reactors) that favors the formation of hydrogen gas to drive the reaction forward, and also employs dilution of the feedstock with gases such as helium, nitrogen, or steam to lower the partial pressure of any hydrogen that is formed in the reaction. Alternatively, the reaction may be conducted under reduced pressure (e.g., from 0.1 to 0.7 atm) to effect reduction of the partial pressure of hydrogen in the reaction, promoting the formation of products. In a second type of hydrogenation, exothermic dehydrogenation, the catalysts typically function in the absence of oxygen, minimizing the formation of oxidized products (e.g., methacrolein and methacrylate, when the feedstock comprises butenes). Oxidative dehydrogenation typically employs mixed metal oxide-based dehydrogenation catalysts (typically containing molybdenum, vanadium, or chromium), lower temperatures (300-500° C.), and a fixed- or fluidized-bed reactor configuration. The process may include the addition of oxygen to the reaction to drive the reaction. Introduced oxygen reacts with produced hydrogen to form water, thus reducing the partial pressure of hydrogen in the reactor and favoring the formation of additional products. Both types of dehydrogenation reactions are applicable to the invention described herein. In some embodiments wherein hydrogen production is desired, endothermic dehydrogenation may be used and reactions conditions may be optimized to maximize hydrogen capture (e.g., for subsequent use in hydrogenation reactions or unit operation as described herein).

The selectivity of dehydrogenation catalysts towards olefins that can accommodate a second olefinic bond can be used to prepare dienes (e.g., butadiene), or alternatively used as a method of purifying the olefin mixture (e.g. by facilitating separation of a diene from unreactive mono-olefins). For example, as described herein, the dehydration of isobutanol typically produces isobutene and both 1- and 2-butenes. Treatment of this product mixture with a dehydrogenation catalyst selectively converts the 1- and 2-butenes—but not isobutene—to butadiene. It is possible that some skeletal rearrangement of the isobutene occurs during the dehydrogenation reaction, but this rearranged material generally is dehydrogenated to form butadiene. After complete dehydrogenation (which may require recycling unreacted butenes back to the dehydrogenation feedstock), the butadiene and unreacted isobutene can be readily separated by extractive distillation of the butadiene, to produce high purity (about 80-100%, e.g., >about 80%, >about 85%, >about 90%, >about 95%, >about 98%, >about 99%, or >about 99.8%) isobutene and butadiene streams suitable e.g. for use as a monomer feedstock for polymerization.

Renewable linear butenes are readily dehydrogenated to renewable butadiene. Accordingly, in the process of the present invention, a portion of the linear butenes produced by dehydration of renewable isobutene can be dehydrogenated to 1,3-butadiene. Under typical linear butene dehydrogenation conditions, isobutene is relatively inert. Accordingly, in various embodiments of the process, butadiene can be pro-

duced by dehydrogenation of mixtures of butenes containing both linear butenes and isobutene. In some embodiments, it may be desirable to remove isobutene from the dehydration product/dehydrogenation feedstock prior to the dehydration reaction (e.g., such that the dehydration feedstock contains essentially only linear butenes). When a mixture of linear butenes and isobutene is dehydrogenated, the dehydrogenation product stream comprises butadiene, unreacted isobutene, and optionally unreacted linear butenes (e.g., produced under low conversion conditions). In some embodiments, at least a portion of the unreacted linear butenes can be recycled back to the dehydrogenation reactor to further convert linear butenes to butadiene (thereby increasing the overall yield of butadiene), and/or a portion of the unreacted linear butenes can be reacted with at least a portion of the ethylene to form propylene (as described herein). The unreacted isobutene can be separated from butadiene, and at least a portion of the unreacted isobutene can be recycled to a separate isomerization step (e.g., producing linear butenes as shown in FIG. **6**) or portions of the unreacted isobutene can be diverted to other processes (e.g., oligomerization, oxidation, etc. to produce biofuels, acrylates, aromatics, etc.) as described herein. If the unreacted isobutene is isomerized to linear butenes, at least a portion of these linear butenes can be recycled back to a dehydrogenation step to produce additional butadiene, or alternatively diverted to other processes such as disproportionation with ethylene to produce additional propylene, alkylation of aromatics, etc.

In still other embodiments, the mixed butenes can be oligomerized over an acidic ion exchange resin under conditions which selectively convert isobutene to isooctene (e.g. using the methods of Kamath R S et al, Industrial Engineering and Chemistry Research 2006, 45, 1575-1582), but leave the linear butenes essentially unreacted, thereby providing a substantially isobutene-free mixture of linear butenes (containing e.g., less than about 1% isobutene, or less than about 0.9%, less than about 0.8%, less than about 0.7%, less than about 0.6%, less than about 0.5%, less than about 0.4%, less than about 0.3%, less than about 0.2%, or less than about 0.1%, including ranges and subranges thereof). Some or all of the essentially isobutene-free renewable linear butenes can then be reacted in the presence of a dehydrogenation catalyst to form renewable butadiene. In still other embodiments, isobutene can be removed from a mixed butene stream by, e.g., selective oxidation of isobutene in the mixed stream to form, e.g., tert-butanol and/or methyl tert-butyl ether.

In another embodiment, the amount of 1- and 2-butenes produced in the dehydration of isobutanol can be increased up to the equilibrium amount accessible at the reaction temperature (see, e.g., FIG. **3**). For example, in some embodiments, dehydration catalysts are selected such that at 350° C., the dehydration of isobutanol produces a mixture comprising about 50% isobutene and about 50% of 1- and 2-butenes. At least a portion of the resulting mixture can be treated with a dehydrogenation catalyst to produce butadiene from isobutanol at up to about 50% yield.

In various embodiments the isobutene can be removed from the mixture of linear butenes prior to dehydrogenation, or alternatively, if the dehydrogenation conditions and catalyst are selected to minimize any undesired side reactions of the isobutene, the isobutene can removed from the product stream after the dehydrogenation reaction step. In other embodiments, a portion or all of the isobutene can be diverted to form other valuable hydrocarbons (e.g., oligomerized to form isooctenes/isooctanes for biofuels, dehydrocyclized to form aromatics for fuels, phthalates, etc.). The isobutene can also be rearranged to linear butenes (1- and 2-butenes), which can then be recycled back to the dehydrogenation reaction step to form additional butadiene, thereby increasing the effective yield of butadiene to above 50% relative to feed isobutanol. If all of the isobutene is recycled, the effective yield of butadiene in various processes of the present invention can approach about 100%. However, as some cracking and "coking" may occur during the dehydrogenation, butadiene yields for the process of the present invention can be about 90% or more (e.g., about 95% or more, or about 98% or more, or any other value or range of values therein or thereabove). The rearrangement of isobutene can be carried out in a separate isomerization step (e.g., in a separate isomerization reactor) after removing the butadiene from the dehydrogenation product, or can be carried out in-situ during the dehydrogenation reaction by appropriate selection of catalyst (or by use of a suitable catalyst mixture) in the dehydrogenation reactor. For example, dehydration catalysts can be selected which also catalyze rearrangement of isobutene to linear isobutenes, or the dehydration catalyst can be mixed with an isomerization catalyst. A few representative acid catalysts suitable for rearranging isobutene include zeolites such as CBV-3020, ZSM-5, β Zeolite CP 814C, ZSM-5 CBV 8014, ZSM-5 CBV 5524 G, and YCBV 870; fluorinated alumina; acid-treated silica; acid-treated silica-alumina; acid-treated titania; acid-treated zirconia; heteropolyacids supported on zirconia, titania, alumina, silica; and combinations thereof.

In particular embodiments, the isobutene is substantially removed from the product stream after the dehydration reaction step in order to provide a feed stream for the dehydrogenation reaction step which is substantially free of isobutene (e.g., the butene component of the dehydrogenation feed stream comprises substantially only linear butenes). By "substantially removed" we mean that isobutene has been removed from the indicated feed or product stream such that after removal, the isobutene in the feed or product stream comprises less than about 5% (e.g., less than about 4%, less than about 3%, less than about 2%, or less than about 1%, or any other value or range of values therein or therebelow) of the butenes in the indicated feed or product stream. By "substantially only" in reference to the composition of the dehydrogenation feed stream, we mean that the linear butenes comprise at least about 95% (e.g., at least about 96%, at least about 97%, at least about 98%, at least about 99%, or any other value or range of values therein or thereabove) of the butenes in the dehydrogenation feed stream.

In one embodiment, renewable butadiene may be prepared from renewable isobutanol produced by fermentation as described herein. The isobutanol thus produced is then dehydrated under conditions (as described herein) to maximize the yield of linear butenes (e.g., heterogeneous acidic catalysts such as γ-alumina at about 350° C.). The resulting mixture of ~1:1 linear butenes/isobutene is then contacted with a dehydrogenation catalyst (e.g., chromium-oxide treated alumina, platinum- and tin-containing zeolites and alumina, cobalt- and molybdenum-containing alumina, etc. at about 450-600° C.) to form a mixture of butadiene and unreacted isobutene. In a specific embodiment, the dehydrocyclization catalyst is a commercial catalyst comprising chromium oxide on an alumina support. The remaining isobutene can then be isomerized to linear butenes as described herein, and recycled for dehydrogenation in order to produce additional butadiene (thereby increasing the effective yield of butadiene), or used as a raw material for other processes or materials as described herein.

Higher Olefins

C_5 and higher molecular weight olefins can also be prepared by the process of the present invention from renewable

isobutanol and/or renewable ethanol by various methods, using a variety of different reactions used individually or in combination. For example, renewable butenes can be converted to renewable C_5 olefins by, for example by hydroformylation by reacting renewable butenes (e.g., renewable isobutene) with formaldehyde (which can be renewable formaldehyde, e.g., prepared from methanol produced from biomass by thermochemical processes) or CO and H_2, in the presence of an acidic catalyst (e.g., via the Prins reaction, see FIG. 6). Renewable pentenes, hexenes and higher molecular weight olefins and can also be prepared as co-products from the metathesis of ethylene and butene mixtures as described herein (e.g., by the disproportionation of isobutene and 1-butene to form ethylene and methylpentene(s), the disproportionation of 2 equivalents of isobutene to form dimethylbutene(s), etc.). By varying the relative amounts of ethylene and the various butene isomers fed to the metathesis reaction and the metathesis reaction conditions (e.g., temperature, pressure, catalyst, residence time, etc., the metathesis product stream can be accordingly adjusted to provide desired amounts of ethylene, propylene, butenes, and C_5 and higher olefins. In particular, higher concentrations of isobutene and/or 1-butene in the metathesis feedstock would favor higher levels of C_5 and higher molecular weight olefins.

Renewable C_5 olefins (e.g., isopentene, 3-methyl-1-butene and 2-methyl-2-butene, etc.) can then be converted to, e.g., isoprene using a dehydrogenation catalyst, under conditions similar to those used to convert butenes to butadiene as described above.

Alternatively, or in addition to the processes for preparing olefins described herein, higher molecular weight olefins can be prepared by oligomerization of lower molecular weight olefins. The term "oligomerization" or "oligomerizing" refer to processes in which activated olefins are combined with the assistance of a catalyst to form larger molecules called oligomers. Oligomerization refers to the combination of identical olefins with one another (e.g., ethylene, isobutene, propylene, pentenes, hexenes, etc.) as well as coupling of different alkenes (e.g., isobutene and propylene), or the combination of an unsaturated oligomer with an olefin. For example, isobutene can be oligomerized by an acidic catalyst to form eight-carbon oligomers (dimers) such as isooctene (e.g., trimethylpent-1-enes and trimethylpent-2-enes) and/or twelve-carbon oligomers (trimers) such as 2,2,4,6,6-pentamethylhept-3-ene, 2,4,4,6,6-pentamethylhept-1-ene. Similarly, oligomers of other monomers can produce higher molecular weight oligomers. In other embodiments, controlled oligomerization of propylene can produce dimers (e.g., hexenes), trimers (e.g., nonenes), etc. Similarly, pentenes, hexenes, or other monomers may be combined in a controlled fashion to provide oligomers having a desired number of carbon atoms. Furthermore, mixed cross-coupling or oligomerization is also possible. For example, propylene and butenes may be oligomerized to provide, e.g., heptenes, decenes, etc.

Heterogeneous or homogenous oligomerization catalysts can be used in the process of the present invention (see, e.g., G. Busca, "Acid Catalysts in Industrial Hydrocarbon Chemistry" *Chem Rev* 2007 (107) 5366-5410. Of the many methods for oligomerizing alkenes, the most relevant processes for the production of fuels and fine chemicals generally employ acidic solid phase catalysts such as alumina and zeolites (see, e.g., U.S. Pat. Nos. 3,997,621; 4,663,406; 4,612,406; 4,864,068; and 5,962,604).

Various methods can be used for controlling the molecular weight distribution of the resulting oligomers, including methods which form primarily dimers including isooctene (see, e.g., U.S. Pat. No. 6,689,927), trimers (see, e.g., PCT Pat. Appl. Pub. No. WO 2007/091862), and tetramers and pentamers (see, e.g., U.S. Pat. No. 6,239,321). Typical methods for controlling oligomer molecular weight include the addition of alcohols such as t-butanol and diluents such as paraffins. Additionally, higher molecular weight oligomers and polymers can be formed using similar catalysts reacting under different conditions. For example, low molecular weight polyisobutylene (up to 20,000 Daltons) can be produced using a boron trifluoride complex catalyst (see, e.g., U.S. Pat. No. 5,962,604).

If a mixture of different olefins produced in any of the processes described herein is oligomerized, the resulting oligomer mixture comprises the corresponding addition products formed by the addition of two or more olefins, which can be the same or different. For example if a mixture of propene and butenes is oligomerized, the product can comprise "binary" or "dimer" addition products such as hexenes, heptenes, octenes; "ternary" or "trimer" addition products such as nonenes, decenes, undecenes, dodecenes, etc.

The renewable unsaturated aliphatic compounds prepared by oligomerization in the process of the present invention generally have, on average, one carbon-carbon double bond per molecule. However, by selecting appropriate reaction conditions (e.g., catalyst identity, residence time, temperature, pressure, etc.), the oligomers formed can have two or more carbon-carbon double bonds, e.g., via dehydrodimerization. On average, the product of the oligomerizing step of the process of the present invention has less than about two double bonds per molecule. In some embodiments, the product oligomer has less than about 1.5 double bonds per molecule. In most embodiments, the unsaturated aliphatic compounds (alkenes) have on average one double bond. Any of the olefins produced by the process of the present invention can be converted to other compounds, for example hydrogenated to form the corresponding saturated hydrocarbons, oxidized to the corresponding alcohol, aldehyde, carboxylic acid, homologated with heteroatoms, etc. using methods known in the art for transforming carbon-carbon double bonds to other functional groups.

The term "oligomerization" can also include reactions of olefins with aromatic hydrocarbons in the presence of an oligomerization catalyst (also termed "alkylation"). Catalysts specifically intended or optimized for the alkylation of aromatics are also termed alkylation or alkylating catalysts, and catalysts specifically intended or optimized for oligomerization of alkenes are termed oligomerization catalysts. Oligomerization and alkylation can, in some embodiments, be carried out simultaneously in the presence of a single catalyst capable of catalyzing both reactions, or in other embodiments, can be carried out as separate reactions using separate oligomerization and alkylation catalysts. For example, benzene can be reacted with isobutylene in the presence of an oligomerization catalyst as described herein to form t-butylbenzene or di-t-butylbenzenes. Similarly, toluene can be reacted in the presence of an oligomerization catalyst and isobutylene to form t-butylmethylbenzenes, etc.

The alkylation of aromatics can be carried out using industrially available catalysts such as mineral acids (e.g., phosphoric acid) and Friedel-Crafts catalysts (e.g., $AlCl_3$-HCl), for example, to alkylate renewable benzene (prepared as described herein) with renewable ethylene or renewable propylene to produce renewable ethyl benzene and cumene, respectively. Renewable ethyl benzene and cumene can then be used as starting materials for the production of renewable phenol and renewable styrene, e.g., using the methods described in *Catalysis Review* 2002, (44) 375. Alternatively, solid acid catalysts such as zeolite-based catalysts can be used

to catalyze the direct alkylation of renewable benzene with renewable propylene or ethylene.

For more highly reactive olefins (reactivity typically increases with increasing length of the olefin chain) oligomerization of the olefin can compete with alkylation of the aromatic, and thus in some embodiments, high aromatic to olefin ratios may be used to minimize formation of olefin oligomers (where such oligomers are undesired) and favor production of alkylated aromatics. Renewable benzene, toluene and xylene can be alkylated with renewable propylene or isobutylene to produce heavier aromatic compounds that are suitable for renewable jet fuel (see, e.g., *Ind. Eng. Chem. Res.* 2008 (47) 1828).

Furthermore, since aromatic alkylation conditions are typically similar to oligomerization conditions, both steps can be performed in one reactor or one reaction zone by reacting a stream of renewable aromatics with renewable alkenes in the presence of a suitable catalyst to provide a mixture of olefin oligomers and alkyl aromatics suitable for use in transportation fuels (e.g., "Jet A" type fuel). Under excess olefin conditions (e.g., low aromatic/olefin ratios), both aromatic alkylation and oligomerization will take place. Alternatively, it is well known that alcohols can also act as alkylating agents under acid catalytic conditions. Accordingly, in other embodiments, aromatics can be alkylated with renewable ethanol or renewable isobutanol under excess alcohol conditions (e.g., dehydration of the alcohol and subsequent oligomerization occur in the presence of aromatics, resulting in alkylation of aromatics). In still other embodiments, oligomerization/aromatic alkylation with propylene or butenes and one or more aromatics can be carried in the presence of an acid catalyst in one reaction zone or in one reactor having two or more reaction zones. In particular embodiments, ethanol or isobutanol can be used as alkylating agents for aromatics in the presence of an acid catalyst in one reaction zone.

Aromatics

Renewable aromatic compounds can be produced from renewable alcohols and olefins, for example, using the methods described in U.S. Pat. Nos. 3,830,866, 3,830,866, and 6,600,081. In particular, renewable aromatics can be readily produced from renewable olefins by dehydrocyclization. For example, renewable propylene dimers (C_6 olefins) produced as described herein can dehydrocyclized to form renewable benzene. Similarly; renewable butene dimers produced as described herein can be dehydrocyclized to C_8 aromatics such as xylenes (particularly p-xylene as described in U.S. Ser. No. 12/899,285) and ethylbenzene. Since olefins are more reactive than the primarily saturated alkanes traditionally used in petroleum refineries to produce aromatics, milder reaction conditions can be used in the processes of the present invention, resulting in improved selectivity for a desired single product (e.g., p-xylene). Alkyl substituted aromatics can alternatively be prepared by alkylation of unsubstituted or substituted aromatics (e.g., benzene or toluene) with low molecular weight olefins (e.g., ethylene) using an appropriate alkylation catalyst.

In the present integrated process(es), the selectivity for p-xylene in an aromatic fraction relative to other aromatic products can be greater than about 90% (e.g., greater than about 95%, greater than about 98%, or any other value or range of values therein or thereabove), using, for example, renewable isooctene as a starting material. The resulting product contains only negligible amounts of renewable benzene and toluene, and predominately comprises xylene(s), from which renewable p-xylene can be recovered at very high purity (e.g., greater than about 90%, greater than about 95%, greater than about 98%, or any other value or range of values therein or thereabove). As previously described herein, appropriate conditions (e.g., catalyst identity, temperature, pressure, residence time, etc.) may be selected to favor formation of, e.g., p-xylene over other xylene isomers.

In alternative embodiments of the process of the present invention, renewable aromatics benzene, toluene, and xylene (BTX) may be produced by the dehydrocyclodimerization and dehydration of renewable alkanes, e.g. isobutane, prepared from renewable alcohols, e.g. isobutanol, reacted with a hydrotreating catalyst. The hydrodeoxygenation process can be carried out over, e.g., Co/Mo, Ni/Mo or both catalysts in the presence of hydrogen at moderate temperatures (e.g., ~150° C.). When isobutanol is used as a starting material in this reaction, the reaction may be highly selective (~90%) for isobutane with high (e.g., more than 95%) conversion.

The renewable alkenes, e.g., propylene or isobutylene, formed by the process of the present invention can also be aromatized using various catalysts, for example zeolite catalysts, e.g. H-ZSM-5 (*Ind. Eng. Chem. Process Des. Dev.* 1986 (25) 151) or GaH-ZSM-5 (*Applied Catalysis* 1988 (43) 155), which sequentially oligomerize the feed olefins, cyclize the oligomerized olefins to naphthenes, and dehydrate the naphthenes to the corresponding aromatic compounds. Alternatively, a metal oxide catalyst can be used in presence of molecular oxygen. This latter type of catalyst dimerizes the olefin to the corresponding diene, which is further cyclized to the corresponding aromatic compound. Because such aromatization conditions are more severe than oligomerization conditions, these two processes are generally carried out as separate process steps.

In some embodiments, the production of renewable aromatics from renewable propylene or isobutylene is achieved according to one of the following processes:

Aromatization of light olefins using zeolites, e.g. H-ZSM-5 or GaH-ZSM-5:

$$C_3 \rightarrow C_6\text{-}C_8 \text{ Aromatics}$$

$$C_4 \rightarrow C_6\text{-}C_8 \text{ Aromatics}$$

Oxidative dehydrodimerization of light olefins using metal oxide/O_2:

$$2C_3H_6 \rightarrow C_6H_{12} \rightarrow \text{benzene} + H_2O$$

$$2C_4H_8 \rightarrow C_8H_{14} \rightarrow \text{p-xylene} + H_2O$$

Dimerization of isobutylene to isooctene followed by its aromatization using eta-alumina doped with Cr, Zr, and other elements:

$$2i\text{-}C_4H_8 \rightarrow i\text{-}C_8H_{16} \rightarrow \text{p-xylene} + 3H_2$$

In most embodiments, however, it is desirable to dehydrocyclize under reducing conditions in order to produce hydrogen as a co-product. The hydrogen produced in the dehydrocyclization reaction can then be used to reduce olefins, particularly isooctene or trimethylheptenes, to the corresponding saturated hydrocarbons which are useful as transportation fuels or fuel additives.

Hydrogenation

Many hydrogenation catalysts are effective, including (without limitation) those containing as the principal component iridium, palladium, rhodium, nickel, ruthenium, platinum, rhenium, compounds thereof, combinations thereof, and the supported versions thereof.

When the hydrogenation catalyst is a metal, the metal catalyst may be a supported or an unsupported catalyst. A supported catalyst is one in which the active catalyst agent is deposited on a support material e.g. by spraying, soaking or

physical mixing, followed by drying, calcination, and if necessary, activation through methods such as reduction or oxidation. Materials frequently used as supports are porous solids with high total surface areas (external and internal) which can provide high concentrations of active sites per unit weight of catalyst. The catalyst support may enhance the function of the catalyst agent: and supported catalysts are generally preferred because the active metal catalyst is used more efficiently. A catalyst which is not supported on a catalyst support material is an unsupported catalyst.

The catalyst support can be any solid, inert substance including, but not limited to, oxides such as silica, alumina, titania, calcium carbonate, barium sulfate, and carbons. The catalyst support can be in the form of powder, granules, pellets, or the like. A preferred support material of the present invention is selected from the group consisting of carbon, alumina, silica, silica-alumina, titania, titania-alumina, titania-silica, barium, calcium, compounds thereof and combinations thereof. Suitable supports include carbon, SiO_2, $CaCO_3$, $BaSO_2$ TiO_2, and Al_2O_3. Moreover, supported catalytic metals may have the same supporting material or different supporting materials.

In one embodiment, the support is carbon. Further useful supports are those, including carbon, that have a surface area greater than 100-200 m^2/g. Other useful supports are those, such as carbon, that have a surface area of at least 300 m^2/g. Commercially available carbons which may be used include those sold under the following trademarks: Bameby & Sutcliffe™, Darco™, Nuchar™, Columbia JXN™, Columbia LCK™, Calgon PCB™, Calgon BPL™, Westvaco™, Norit™ and Barnaby Cheny NB™. The carbon can also be commercially available carbon such as Calsicat C, Sibunit C, or Calgon C (commercially available under the registered trademark Centaur®).

Particular combinations of catalytic metal and support system suitable for use in the methods of the present invention include nickel on carbon, nickel on Al_2O_3, nickel on $CaCO_3$, nickel on TiO_2, nickel on $BaSO_4$, nickel on SiO_2, platinum on carbon, platinum on Al_2O_3, platinum on $CaCO_3$, platinum on TiO_2, platinum on $BaSO_4$, platinum on SiO_2, palladium on carbon, palladium on Al_2O_3, palladium on $CaCO_3$, palladium on TiO_2, palladium on $BaSO_4$, palladium on SiO_2, iridium on carbon, iridium on Al_2O_3, iridium on SiO_2, iridium on $CaCO_3$, iridium on TiO_2, iridium on $BaSO_4$, rhenium on carbon, rhenium on Al_2O_3, rhenium on SiO_2, rhenium on $CaCO_3$, rhenium on TiO_2, rhenium on $BaSO_4$, rhodium on carbon, rhodium on Al_2O_3, rhodium on SiO_2, rhodium on $CaCO_3$, rhodium on TiO_2, rhodium on $BaSO_4$, ruthenium on carbon, ruthenium on Al_2O_3, ruthenium on $CaCO_3$, ruthenium on TiO_2, ruthenium on $BaSO_4$, and ruthenium on SiO_2.

Raney metals or sponge metals are one class of catalysts useful for the present invention. A sponge metal has an extended "skeleton" or "sponge-like" structure of metal, with dissolved aluminum, and optionally contains promoters. The sponge metals may also contain surface hydrous oxides, absorbed hydrous radicals, and hydrogen bubbles in pores. Sponge metal catalysts can be made by the process described in U.S. Pat. No. 1,628,190, the disclosure of which is incorporated herein by reference.

In various embodiments, the sponge metals include nickel, cobalt, iron, ruthenium, rhodium, iridium, palladium, and platinum. Sponge nickel or sponge cobalt are particularly useful as catalysts. The sponge metal may be promoted by one or more promoters selected from the group consisting of Group IA (lithium, sodium, and potassium), IB (copper, silver, and gold), IVB (titanium and zirconium), VB (vanadium), VIB (chromium, molybdenum, and tungsten), VIIB (manganese, rhenium), and VIII (iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum) metals. The promoter can be used in an amount useful to give desired results. For example, the amount of promoter may be any amount less than 50% by weight of the sponge metal, 0 to 10% by weight, 1 to 5% by weight, or any other value or range of values therein.

Sponge nickel catalysts contain mainly nickel and aluminum. The aluminum is typically in the form of metallic aluminum, aluminum oxides, and/or aluminum hydroxides. Small amounts of other metals may also be present either in their elemental or chemically bonded form, such as iron and/or chromium, and may be added to the sponge nickel to increase activity and selectivity for the hydrogenation of certain groups of compounds. In certain embodiments, chromium and/or iron promoted sponge nickel is employed as a catalyst.

Sponge cobalt catalysts also contain aluminum and may contain promoters. In certain embodiments, the promoters are nickel and chromium, for example in amounts of about 2% by weight based on the weight of the catalyst. Examples of suitable sponge metal catalysts include Degussa BLM 112W, W. R. Grace Raney ® 2400, Activated Metals A-4000™, and W. R. Grace Raney ® 2724.

As stated above, useful catalytic metals include component iridium, palladium, rhodium, nickel, ruthenium, platinum, rhenium; and useful support materials include carbon, alumina, silica, silica-alumina, titania, titania-alumina, titania-silica, barium, calcium, particularly carbon, SiO_2, $CaCO_3$, $BaSO_2$ and Al_2O_3. A supported catalyst may be made from any combination of the above named metals and support materials. A supported catalyst may also, however, be made from combinations of various metals and/or various support materials selected from subgroup(s) of the foregoing formed by omitting any one or more members from the whole groups as set forth in the lists above. As a result, the supported catalyst may in such instance not only be made from one or more metals and/or support materials selected from subgroup(s) of any size that may be formed from the whole groups as set forth in the lists above, but may also be made in the absence of the members that have been omitted from the whole groups to form the subgroup(s). The subgroup(s) formed by omitting various members from the whole groups in the lists above may, moreover, contain any number of the members of the whole groups such that those members of the whole groups that are excluded to form the subgroup(s) are absent from the subgroup(s). For example, it may be desired in certain instances to run the process in the absence of a catalyst formed from palladium on carbon.

The optimal amount of the metal in a supported catalyst depends on many factors such as method of deposition, metal surface area, and intended reaction conditions, but in many embodiments can vary from about 0.1 wt % to about 20 wt % of the whole of the supported catalyst (catalyst weight plus the support weight). In particular embodiments, the catalytic metal content range is from about 0.1 wt % to about 10 wt % by weight of the whole of the supported catalyst. In yet other embodiments, the catalytic metal content range is from about 1 wt % to about 7 wt % by weight of the whole of the supported catalyst. Optionally, a metal promoter may be used with the catalytic metal in the method of the present invention. Suitable metal promoters include: 1) those elements from groups 1 and 2 of the periodic table: 2) tin, copper, gold, silver, and combinations thereof: and 3) combinations of group 8 metals of the periodic table in lesser amounts.

Temperature, solvent, catalyst, pressure and mixing rate are all parameters that may affect hydrogenation. The rela-

tionships among these parameters may be adjusted to effect the desired conversion, reaction rate, and selectivity in the reaction of the process.

In one embodiment, the hydrogenation temperature is from about 25° C. to 350° C. (e.g., from about 50° C. to about 250° C., or any other value or range of values therein), and in certain embodiments, from about 50° C. to 200° C. The hydrogen pressure can be about 0.1 to about 20 MPa, or about 0.3 to 10 MPa, and in certain embodiments from about 0.3 to about 4 MPa. The reaction may be performed neat or in the presence of a solvent. Useful solvents include those known in the art of hydrogenation such as hydrocarbons, ethers, and alcohols (where the alcohols and ethers, or hydrocarbon solvents can be renewable). In particular embodiments, alcohols such as lower alkanols like methanol, ethanol, propanol, butanol, and pentanol are useful. Selectivities in the range of at least 70% are attainable in the process of the present invention, for example selectivities of at least 85%, at least 90%, or any other value or range of values therein or thereabove. Selectivity is the weight percent of the converted material that is a saturated hydrocarbon where the converted material is the portion of the starting material that participates in the hydrogenation reaction.

Upon completion of the hydrogenation reaction, the resulting mixture of products may be separated by a conventional method, such as for example, by distillation, by crystallization, or by preparative liquid chromatography.

Products

Embodiments of the present invention also relate to renewable hydrocarbon feedstocks and products produced according to the integrated processes described herein. Certain exemplary renewable hydrocarbon feedstocks produced according to the present processes, and products formed therefrom according to the integrated methods described herein, are described below.

Ethylene

The renewable ethylene produced by the processes of the present invention can be used to prepare other hydrocarbons such as propylene, styrene (e.g., by alkylation of benzene) etc. as described herein. Alternatively, at least a portion of the ethylene can be used to prepare other value-added products such as polyethylene (e.g., polyethylene homopolymers and copolymers, waxes, etc.); ethylene oxide (which itself can be used to prepare other products such as polyethylene oxide polymers and copolymers, ethylene glycol, ethylene oxide-containing specialty chemicals such as surfactants, detergents, etc.); halogenated hydrocarbons such as ethylene dichloride, ethylene chloride, ethylene dibromide, chloroethylene, trichloroethylene, and polymers and copolymers derived from these halogenated hydrocarbons (e.g. PVC, PVdC, etc.); propanal (e.g., by hydroformylation) or propylene (e.g. by metathesis as described herein).

Propylene

The renewable propylene produced by the process of the present invention can be used to prepare a variety of renewable products including renewable polypropylene, renewable ethylene propylene rubbers; renewable propylene oxide and renewable polymers prepared from renewable propylene oxide such as polypropylene oxide and polypropylene oxide/polyethylene oxide copolymers, polypropylene oxide polyols for polyurethanes, etc.; renewable aldehydes and ketones such as propanal, acetone, butyraldehyde, isobutyraldehyde, etc.; 2-ethylhexanol and 2-ethylhexanoic acid; aromatics such as cumene and phenol; monomers such acrylic acid, acrylonitrile, and adiponitrile (and derivatives thereof such adipic acid, 1,6-diaminohexane), etc.

Renewable polypropylene can be prepared directly from renewable propylene prepared as described herein using methods and polymerization catalysts known in the art (for example, catalysts and methods described by Hansjorg Sinn and Walter Kaminsky, "Ziegler-Natta Catalysis", *Advances in Organometallic Chemistry* 1980 (18) 99-148 and U.S. Pat. No. 7,563,836). The resulting renewable polypropylene can have any suitable tacticity (e.g., atactic, isotactic, syndiotactic, eutactic) depending on the nature of the catalyst used and polymerization conditions. In addition, renewable propylene prepared as described herein can be copolymerized with other suitable monomers such as ethylene and/or other olefins to prepare thermoplastic polymers (e.g., thermoplastic elastomers), at least a portion of which may be renewable. For example, copolymers prepared with the renewable propylene prepared as described herein can be prepared by the methods described in U.S. Pat. No. 5,272,236.

Renewable polypropylene is particularly useful as a replacement for petroleum derived polypropylene, which is used for a wide variety of products including backing and non-woven fiber sheets used in diapers, as a component of hot melt adhesives (e.g., co-monomers in polyolefin hot melt adhesives), as a component of pressure sensitive adhesives, in extruded/thermoformed/injection molded products, fibers, blown films, cast films, foams, etc., as components and/or copolymers in packaging (films, caps and closures, bottles, containers, etc.), fibers (e.g., nonwoven sheets, carpet fibers, textiles, tape and strapping, staple fibers, bulk and continuous filament, etc.), as components of toys, housewares (e.g., plastic utensils, cups, storage containers, etc.), packing and insulating foams, automotive components (e.g., interior and exterior trim, bumper fascia, etc.), tools (e.g., handles, power tool enclosures, knobs, etc.), electronic enclosures (e.g., mobile phones, TVs, battery cases, etc.), ropes and cables, wire cladding, pipes, etc.

Alternatively, or in addition, renewable polypropylene prepared as described herein can be used to prepare other monomers such as propylene oxide. Renewable propylene oxide can be prepared by a variety of methods, including oxidation with cumene hydroperoxide (e.g., as described in EP 1382602 or U.S. Pat. No. 7,273,941) or oxidation with hydrogen peroxide (e.g. in the presence of a titanium or vanadium silicalite catalyst as described in U.S. Pat. No. 7,273,941 or WO 97/47613). Other methods for oxidizing propylene to propylene oxide known in the art can also be used. The renewable propylene oxide thus formed can then be polymerized or copolymerized using conventional methods (e.g., via base-catalyzed polymerization with a base such as KOH, with a salen cobalt catalyst, etc., using a monofunctional initiator such as an alcohol, ethylene glycol, etc., or a polyfunctional initiator such as glycerol, pentaerythritol, sorbitol, etc.) to provide at least partially renewable polypropylene oxide or at least partially renewable polypropylene oxide copolymers (e.g., ethylene oxide/propylene oxide copolymers).

If cumene hydroperoxide is used as the oxidizing agent to prepare propylene oxide, the cumene hydroperoxide itself can be prepared from renewable propylene and integrated into the process of the present invention as described herein. For example, renewable cumene hydroperoxide can be prepared by the oxidation of renewable cumene, which in turn can be prepared from by various combinations of olefin oligomerization, dehydrocyclization, and/or alkylation steps as described herein. For example, renewable propylene can be dimerized, then dehydrocyclized to form renewable benzene, which can then alkylated with an additional equivalent of renewable propylene to form renewable cumene (e.g., as described in U.S. Pat. No. 2,860,173 and U.S. Pat. No. 4,008,

290). Alternatively, renewable propylene can be trimerized and dehydrocyclized directly to form renewable cumene (e.g., similar to the methods described in *Ind. Eng. Chem. Process Des. Dev.* 1986 (25) 151; *Applied Catalysis* 1988 (43) 155; or as described in U.S. Pat. No. 3,879,486). The product renewable cumene can then be oxidized to renewable cumene hydroperoxide using known methods.

Renewable cumene hydroperoxide can be used as an oxidizing agent to oxidize renewable propylene to propylene oxide (e.g., as described in EP 1382602), and/or decomposed to form renewable phenol and renewable acetone (e.g., using the method described in U.S. Pat. No. 5,254,751 or U.S. Pat. No. 2,663,735). In some embodiments, the production of renewable cumene hydroperoxide from renewable propylene can be integrated with a process for preparing renewable propylene oxide, renewable phenol, and renewable acetone (e.g., by preparing renewable cumene by the oligomerization-cyclodehydrogenation-alkylation of renewable propylene, then oxidizing the renewable cumene to form renewable cumene hydroperoxide, then contacting additional renewable propylene with the renewable cumene hydroperoxide to form renewable propylene oxide, and decomposing renewable cumene hydroperoxide to form renewable phenol and renewable acetone), as exemplified in FIG. **8**.

The renewable acetone prepared by the decomposition of renewable cumene hydroperoxide can then be used, e.g., as a precursor for methylmethacrylate monomer (via reaction with hydrogen cyanide), a precursor for bisphenol A (via reaction with phenol, e.g., renewable phenol produced in the decomposition of renewable cumene hydroperoxide), or used directly as a renewable industrial solvent. In addition to renewable bisphenol A, the renewable phenol produced by the decomposition of renewable cumene hydroperoxide can be used as a synthetic intermediate in the preparation of, e.g., aspirin, herbicides, cosmetics, sunscreens, etc., and/or as a monomer in the preparation of synthetic resins (phenol/formaldehyde resins such as Bakelite, etc.).

Renewable propylene prepared by the methods disclosed herein can also be converted to oxidized monomers such as renewable acrylic acid, for example by reacting propylene in the vapor phase in the presence of a solid phase catalyst, such as those disclosed in WO 2009/017074, e.g., a two-stage reaction over two different catalyst beds: in the first stage, propylene is oxidized to acrolein using a bismuth molybdate catalyst in a strongly exothermic reaction (at about 370° C.); in the second stage, the acrolein gas is further oxidized to acrylic acid in the gas phase over a molybdenum vanadium oxide catalyst. Alternatively, the renewable propylene can be converted to acrylic acid using the methods of U.S. Pat. No. 6,281,384 (e.g., using a bismuth molybdate multicomponent metal oxide catalyst such as $Mo_{12}CO_{5.5}Bi_{1.0}Fe_{0.8}W_{1.2}Si_{1.2}K_{0.05}O_x$ or a molybdenum vanadate multimetal oxide such as $Mo_{12}V_{4.8}Sr_{0.5}W_{2.4}Cu_{2.2}O_x$); in the presence of a mixed metal oxide catalyst, water, and oxygen using the method of the EP 1201636; or by oxidation in the presence of a mixed metal oxide catalyst as described in JP 07-053448 or WO2000/09260. The resulting renewable acrylic acid can then be polymerized or copolymerized to form renewable polyacrylic acid and polyacrylic acid copolymers, polymerized and crosslinked to form superabsorbent gels e.g. for diapers, esterified to form at least partially renewable acrylic esters (or fully renewable if esterified with renewable alcohols). The at least partially renewable acrylic esters can likewise be polymerized or copolymerized to renewable acrylate ester polymers or copolymers.

Renewable methacrylates can also be formed from renewable propylene, for example by oxycarbonylation of renewable propylene, e.g., using the catalytic process of U.S. Pat. No. 3,907,882 in which the propylene, CO and O_2 are reacted in the presence of a rhenium compound prepared from rhenium (V) chloride, aluminum chloride, lithium chloride, and sodium acetate. Analogously to renewable acrylic acid as described herein, renewable methacrylic acid can be esterified and/or polymerized (or copolymerized) to form an at least partially renewable methacrylic acid (ester) polymer or copolymer.

Renewable acrylonitrile can be prepared, e.g., by reacting renewable propylene in the presence of an ammoxidation catalyst (e.g., a multicomponent metal oxide catalyst comprising Bi, Mo, P, and/or Fe oxides), oxygen and ammonia, for example as described in EP 1201636, U.S. Pat. No. 4,230,640, U.S. Pat. No. 4,267,385, U.S. Pat. No. 3,911,089, and U.S. Pat. No. 5,134,105. The resulting renewable acrylonitrile can then be polymerized or copolymerized (e.g., to form renewable polyacrylonitrile).

Renewable acrylonitrile can also be electrochemically dimerized to form adiponitrile, for example using the methods described in GB 1089707 and U.S. Pat. No. 4,155,818, or catalytically dimerized using the methods described in U.S. Pat. No. 4,841,087 (e.g., wherein 1,4-dicyanobutene is reduced to adiponitrile). The resulting renewable adiponitrile can be hydrolyzed to form renewable adipic acid and/or reduced to form renewable hexamethylene diamine (1,6-diaminohexane). The renewable adipic acid or renewable hexamethylene diamine can be polymerized separately with, respectively an appropriate diamine or diacid (or synthetic equivalents thereof), or polymerized together to form completely renewable nylon 6,6. Alternatively, the renewable adipic acid and hexamethylene diamine can be used in the preparation of other valuable and useful materials such as polyurethanes or plasticizers, as crosslinking agents (e.g., for epoxy resins), etc.

The renewable propylene prepared by the integrated methods described herein can also be converted to renewable acetone or propanal by oxidation using known methods, or converted to renewable C_4 aldehydes, alcohols, and/or acids by hydroformylation, e.g., using the methods of U.S. Pat. No. 3,274,263 or U.S. Pat. No. 2,327,066.

Higher alcohols and acids such as 2-ethylhexanol or 2-ethylhexanoic acid can also be prepared from renewable propylene using similar methods, for example by reacting renewable polypropylene, carbon monoxide, hydrogen and acetic acid (e.g., prepared by oxidation of renewable ethanol) in the presence of a suitable catalyst (e.g., cobalt acetate) using the methods of U.S. Pat. No. 2,691,674. 2-Ethylhexanol acetate can be selectively prepared under such conditions at temperatures of about 250° C. to about 290° C. at pressures of about 500-1500 atmospheres and CO/H_2 ratios of 0.75-1.5. The renewable 2-ethylhexanol acetate can be hydrolyzed to regenerate acetic acid used in the reaction, and the resulting 2-ethylhexanol can be oxidized to 2-ethylhexanoic acid using known methods. Alternatively, 2-ethylhexanol can be prepared by base-catalyzed aldol condensation of n-butyraldehyde using the method of U.S. Pat. No. 5,144,089. In various embodiments, renewable C_4 and C_8 aldehydes, alcohols, acids and acid derivatives (e.g., amides, nitriles, acid chlorides, esters, etc.) can be prepared from renewable propylene by known processes such as hydroformylation, and/or base catalyzed aldol condensation, and/or reduction, and/or oxidation of the appropriate intermediates as shown in FIG. **9**.

The resulting renewable C_4 and C_8 aldehydes, alcohols, acids and acid derivatives can be used for various applica-

tions, for example in the synthesis of phthalate ester plasticizers (2-ethylhexanol), industrial solvents (butanols), specialty chemicals (metal salts of 2-ethylhexanoic acid), etc.

In still other embodiments, renewable ethylene, butenes, propylene and/or higher olefins produced by the present integrated methods may be oligomerized, e.g., as described in U.S. Ser. No. 12/327,723 to provide renewable transportation fuels, e.g., gasoline, jet fuels and/or diesel fuels.

C_4 Oxidized Hydrocarbons

As described above, the process of the present invention provides isobutanol from biomass or CO_2 by, e.g., fermentation or thermochemical methods. Renewable isobutanol can be converted to other butanol isomers by, for example, rearrangement of isobutanol, and/or can be converted to various butyraldehydes, butyric acids and/or butyric acid derivatives by appropriate oxidation or reaction of the corresponding alcohol. However, in some cases (for example to ensure complete utilization of the renewable propylene) it may be desirable to convert a certain portion of the renewable propylene provided by the methods of the present invention to various renewable C_4 aldehydes, alcohols, and/or acids by hydroformylation.

Butenes

As discussed herein, renewable isobutene and linear butenes produced by the process of the present invention can be used as starting materials to produce higher molecular weight renewable olefins and alkanes useful as renewable fuels and fuel additives, or as monomers for the production of polymers and copolymers, such as polybutene and polyisobutylene suitable for use in a variety of applications, for example chemical intermediates for the preparation of engine oil, fuel additives, and greases; an intermediate in the preparation of dispersants such as polybutenyl succinic anhydride; as intermediates in the preparation of sealants and adhesives; modifiers for polymers such as tackifiers for polyethylene and for adhesive polymers; and in hydrogenated form as components of cosmetic formulations.

Butadiene

The renewable butadiene thus obtained can then be converted, for example, to a wide variety of renewable polymers and co-polymers by most known methods of polymerization and used in a multitude of commercial applications. As described herein, renewable butadiene can be polymerized or copolymerized with other monomers (which themselves may be renewable monomers or monomers obtained from conventional, non-renewable sources). For example, very low molecular weight polymers and copolymers of butadiene, called telomers or liquid polybutadiene, can be prepared by anionic polymerization using initiators such as n-butyl lithium, often with co-initiators such as potassium tert-butoxide or tert-amines as described in U.S. Pat. No. 4,331,823 and U.S. Pat. No. 3,356,754. These low molecular weight oligomers (e.g., MW 500-3000) can be used in pressure sensitive adhesives and thermosetting rubber applications. Butadiene can also be co- and ter-polymerized with vinyl pyridine and/or other vinyl monomers (e.g. renewable vinyl monomers) in an emulsion process to form polymers useful in floor polishes, textile chemicals and formulated rubber compositions for automobile tires. Butadiene can also be anionically polymerized with styrene (e.g., renewable styrene) and vinyl pyridine to form triblock polymers as taught in U.S. Pat. No. 3,891,721 useful for films and other rubber applications.

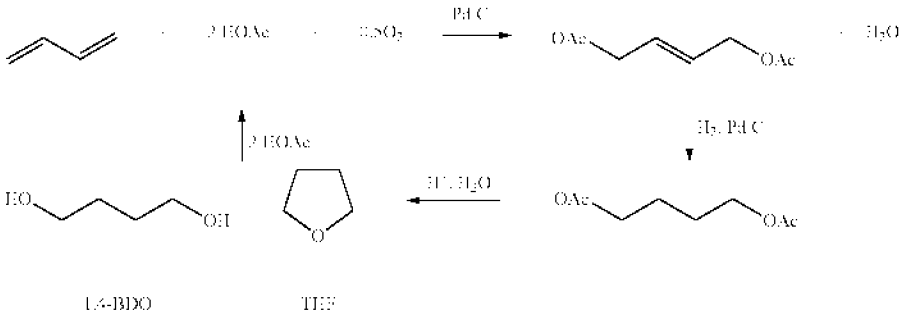
Butadiene and styrene can be sequentially, anionically polymerized in non-polar solvents such as hexane, to form diblock and triblock polymers, also called SB elastomers, ranging from rigid plastics with high styrene content to thermoplastic elastomers with high butadiene content. These polymers are useful for transparent molded cups, bottles, impact modifiers for brittle plastics, injection molded toys as well as components in adhesives. Solution polybutadiene can be prepared from butadiene, also by anionic polymerization, using initiators such as n-butyl lithium in non-polar solvents without utilizing a comonomer. These elastomers are non-crosslinked during the polymerization and can be used as impact modifiers in high impact polystyrene and bulk polymerized ABS resins, as well as in adhesives and caulks. Solution polymerized polybutadiene can also be compounded with other elastomers and additives before vulcanization and used in automobile tires. Emulsion (latex) polymerization can also be used to convert butadiene and optionally, other monomers such a styrene, methyl methacrylate, acrylic acid, methacrylic acid, acrylonitrile, and other vinyl monomers, to polymers having both unique chemical structure and designed physical structure suitable for specific end use applications.

Emulsion polymerization utilizes water as the continuous phase for the polymerization, surfactants to stabilize the growing, dispersed polymer particles and a compound to generate free radicals to initiate the polymerization. Styrene-butadiene emulsion rubber used for automobile tires can be made by this process. Renewable vinyl acids such as acrylic acid and methacrylic acid (as described herein) can be copolymerized in the styrene butadiene rubber. Low levels (0.5-3%) of vinyl acids improve the stability of the latex and can be beneficial in formulated rubber products such as tires, especially when containing polar fillers. Higher levels of acid in rubber latexes, often called carboxylated latex, are used beneficially in paper coating. Latex polymerization is also used to produce rubber toughened plastics and impact modifiers. Impact modifiers made by latex polymerization are also called core-shell modifies because of the structure that is formed while polymerizing the monomers that comprise the polymer.

MBS resins are made by a sequential emulsion process where butadiene (B) and styrene (S) are first polymerized to form the rubber particle core, typically 0.1-0.5 micrometers in diameter, and then methyl methacrylate (M) is polymerized to form a chemically grafted shell on the outer surface of the SB rubber core, for example as taught in U.S. Pat. No. 6,331,580. This impact modifying material is isolated from the latex and blended with plastics to improve their toughness. If acrylonitrile (A) is used in place of the methyl methacrylate, with slight variations in the process, such as disclosed in U.S. Pat. No. 3,509,237 and U.S. Pat. No. 4,385,157, emulsion ABS is the product. Each of these components in ABS (including acrylonitrile) may be renewable, produced by the methods described herein. ABS is used in injection molding and extrusion processes to produce toys, automobile parts, electronic enclosures and house wares. Nitrile rubber is produced in a similar emulsion polymerization process when butadiene and acrylonitrile are copolymerized together to produce a polar elastomer that is very resistant to solvents. Higher butadiene content in the elastomer provides a softer, more flexible product while higher acrylonitrile content results in more solvent resistance. The rubber is isolated from the latex by coagulation and can be fabricated into gloves, automotive hoses, and gaskets where its high resistance to solvents is an advantage.

Renewable butadiene prepared by the process described herein can also be converted to renewable 1,4-butanediol (BDO) and/or renewable tetrahydrofuran (THF), for example using the process described in JP 10-237017 and JP 2001002600 (illustrated below in Scheme 1), in which butadiene is reacted with acetic acid and oxygen in the presence of a palladium catalyst (liquid phase at about 70° C. and 70 bar, using a promoter such as Sb, Bi, Se or Te) to form 1,4-diacetoxy-2-butene, which is then hydrogenated (liquid phase, at about 50° C. and 50 bar over a conventional hydrogenation catalyst such as Pd/C) to 1,4-diacetoxybutane. Acidic hydrolysis of the 1,4-diacetoxybutane (e.g., using an acidic ion exchange resin) provides BDO and THF in high yield.

SCHEME 1:



Renewable BDO and THF can be converted to a variety of renewable products. For example renewable BDO can be reacted with a suitable diisocyanates to form renewable Lycra™ and Spandex™ products, as well as thermoplastic urethane elastomers. Renewable BDO can also be used to form renewable polybutylene terephthalate by reacting renewable BDO with terephthalic acid or terephthalate esters, or can be copolymerized with renewable aliphatic diacids such as adipic acid or succinic acid to form renewable aliphatic polyesters such as polybutylene adipate or polybutylene succinate. In some embodiments the terephthalic acid or terephthalate esters can be renewable, prepared by oxidation of renewable xylene made, e.g., by the method described in U.S. Ser. No. 12/327,723 and U.S. 61/295,886. Renewable BDO can also be used to prepare renewable γ-butyrolactone (GBL), renewable pyrrolidone solvents such as N-methylpyrrolidinone (NMP), renewable N-vinylpyrrolidinone (NVP), etc. as illustrated below in Scheme 2:

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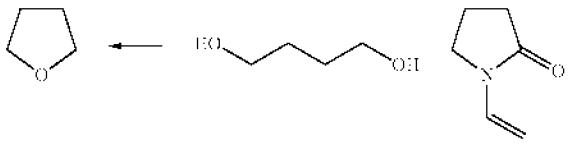
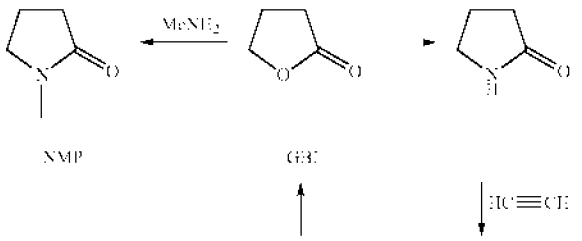


THF 1,4-BDO NVP

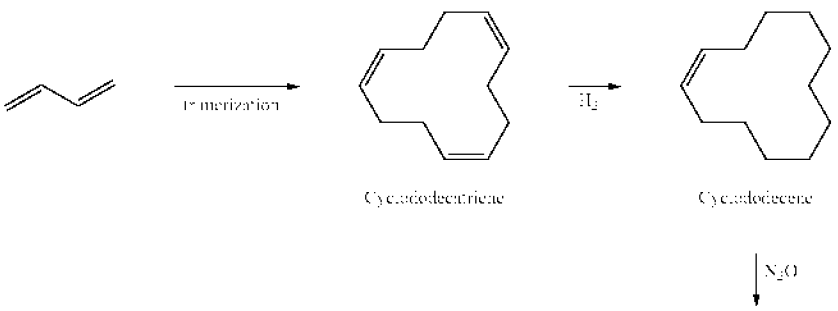
SCHEME 2:



Renewable GBL and NMP can be used as solvents, and renewable NVP can be used in personal care products such as hairspray.

Renewable butadiene prepared by the processes described herein can also be used to form renewable dodecanedioic acid (DDDA), or renewable lauryllactam by forming the oxime of the intermediate cyclododecanone, then rearranging the oxime to lauryllactam (e.g., using the method of U.S. Pat. No. 6,649,757). The lauryllactam can then be polymerized to form renewable nylon-12, as shown below in Scheme 3:

SCHEME 3:



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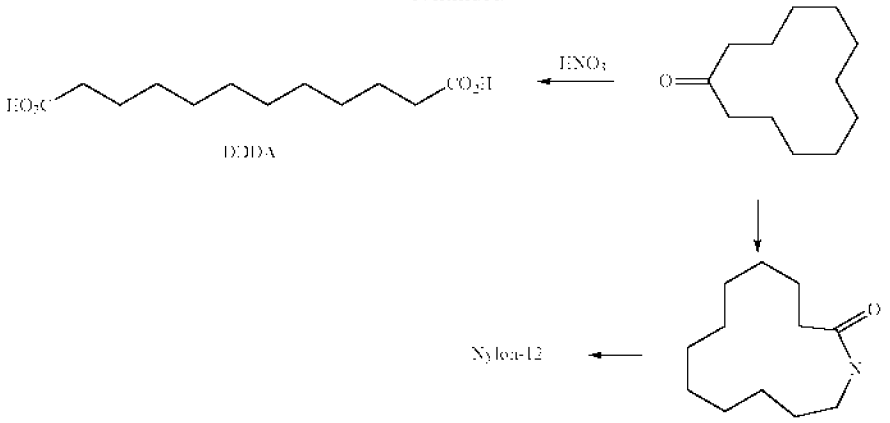
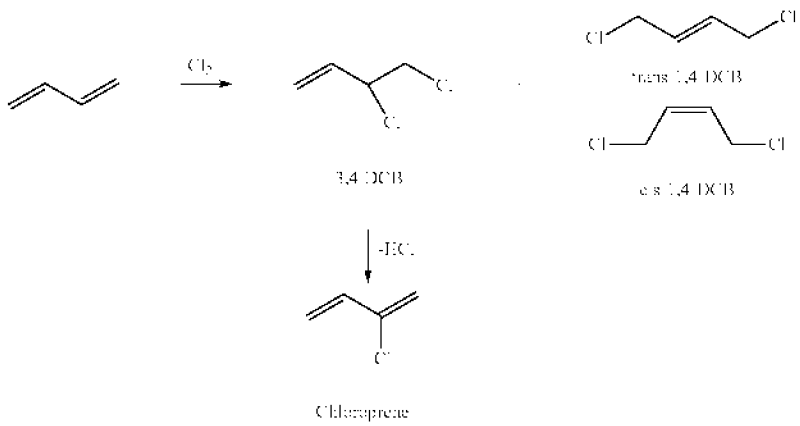


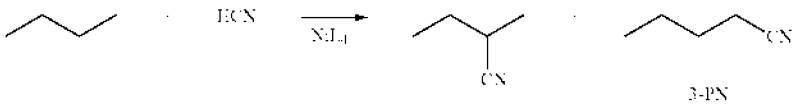
Renewable butadiene prepared by the processes described herein can also be used to prepare renewable chloroprene, which can be polymerized to provide renewable synthetic rubbers. Renewable chloroprene can be prepared by chlorinating renewable butadiene (e.g., free radical, gas phase chlorination with Cl_2 at 250° C. and 1-7 bar to give a mixture of cis and trans-1,4-DCB as well as 3,4-DCB). At butadiene conversions of 10-25%, the selectivity to this mixture of DCBs can be 85-95%. 3,4-dichloro-1-butene (3,4-DCB) can be dehydrochlorinated to form chloroprene (e.g., using dilute alkaline catalysts at 85° C.), as shown below in Scheme 4. The 1,4-DCB by-products can be isomerized to 3,4-DCB using a copper catalyst. In addition, by distilling off the 3,4-DCB during the reaction (b.p. 123° C. vs. 155° C. for the 1,4-isomers), the equilibrium of the reaction can be shifted to provide a selectivity of 95-98%.

SCHEME 4:



Renewable butadiene prepared by the processes described herein can also be used to prepare renewable nylon-6,6 (Scheme 5). For example, renewable nylon-6,6 can be prepared by reacting renewable butadiene with HCN in the presence of a zero valent nickel catalyst to provide adiponitrile. Adiponitrile can be hydrogenated to form hexamethylenediamine (HMD), and hydrolyzed to form adipic acid. The HMD and adipic acid can then be polymerized to form nylon-6,6.

SCHEME 5:



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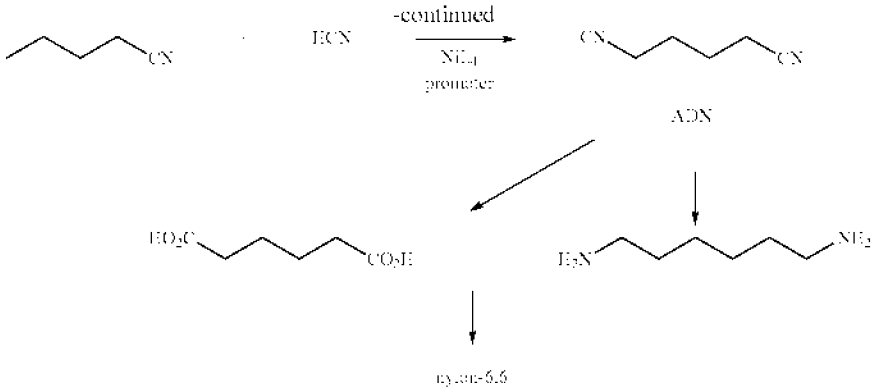
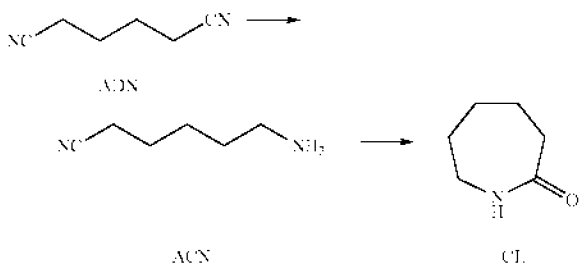


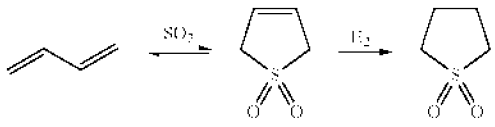
Alternatively, as shown in Scheme 6, renewable adiponitrile can be hydrocyanated and cyclized to renewable caprolactam (CL), e.g., using a doped Raney Ni (using the method of U.S. Pat. No. 5,801,286) and cyclized to CL in the presence of water (using the method of U.S. Pat. No. 5,693,793). The renewable caprolactam can then be polymerized to form renewable nylon-6 using methods known in the art.

SCHEME 6:



Renewable butadiene prepared by the processes described herein can also be used to prepare renewable sulfolene and sulfolane using the method illustrated in Scheme 7:

Scheme 7:



Renewable butadiene prepared by the processes described herein can also be used to prepare renewable styrene, renewable polystyrene, and renewable styrenic polymers (e.g., renewable SBR rubbers). Renewable styrene can be prepared, for example by dimerizing renewable butadiene to form vinylcyclohexene, which can be dehydrogenated in a stepwise fashion to form ethyl benzene (e.g., using the method of WO 2003/070671), then styrene (e.g., using the method of U.S. Pat. No. 4,229,603). Alternatively, vinylcyclohexene can be dehydrogenated directly to styrene. The renewable styrene can be homopolymerized to form renewable polystyrene, copolymerized with renewable butadiene to form SBR rubber, etc.

Renewable butadiene prepared by the processes described herein can also be used to prepare renewable ethylidene norbornene (ENB) for producing completely renewable or partially renewable ethylene-propylene-diene rubber (depending on whether renewable ethylene and/or propylene are used). Renewable ethylene can be prepared by dehydrogenating renewable ethanol (e.g. produced by fermentation or thermochemical methods), and renewable propylene can be prepared, for example by the methods described in U.S. 61/155,029. Renewable ENB can be prepared, for example, by reacting renewable butadiene and dicyclopentadiene in a four-step process. In the first step, dicyclopentadiene is decoupled to cyclopentadiene and reacted with renewable butadiene via Diels-Alder condensation to vinylnorbornene (VNB). This is followed by distillation to obtain refined VNB, which is catalytically isomerized (U.S. Pat. No. 4,720,601) to ENB.

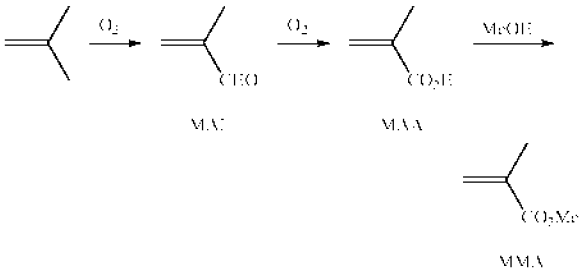
Renewable butadiene prepared by the processes described herein can also be thermally dimerized to form renewable 1,5-cyclooctadiene (COD) using the methods of, e.g., U.S. Pat. No. 4,396,787. Renewable COD can be used in the preparation of renewable ethylene oligomerization catalysts such as $Ni(COD)_2$. Butadiene can also be dimerized to produce 1-octene and 1-octanol.

In other embodiments, the dehydration of 3-methyl-1-butanol produces a mixture of methyl butenes and small amounts of other pentenes which upon treatment with a dehydrogenation catalyst forms primarily isoprene from methylpentenes (e.g. 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene), for example 3-methyl-1-butene, and other pentadienes, such as 1,3-pentadiene, from other pentenes. The pentadienes are separated from each other by distillation. Dehydration catalysts and conditions are optimized to produce varying amounts of specific olefins, and their resulting di-olefins upon treatment with a dehydrogenation catalyst.

The purification of isobutene as described above produces renewable isobutene that meets all current industrial specifications and can be used to manufacture all chemicals and materials currently produced, e.g., from conventional petroleum-based isobutene. For example, renewable or partially renewable polyisobutylene, butyl rubber, methyl methacrylate, isoprene, and other chemicals can be produced by the methods of the present invention. Renewable isobutene can also be oxidized under suitable conditions to provide methacrylic acid and methacrylic acid esters (Scheme 8). Isobutene can be oxidized over suitable metal oxide catalysts (e.g., using the methods described in JP 2005-253415) at temperatures of about 300-500° C. to methacrolein (MAL) which is then further oxidized to methacrylic acid (MMA)

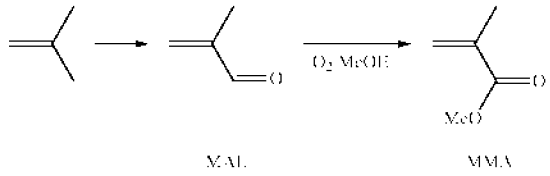
(WO 2003053570) at temperatures of about 350-500° C. The resultant methacrylic acid can be further esterified to methylmethacrylate. The oxidation of isobutene to MMA may also be accomplished in a single step (e.g. as described in WO2003053570).

SCHEME 8:



An alternative process for the preparation of MMA is by the oxidative esterification of MAL to MMA (e.g., as described in U.S. Pat. No. 4,518,796) using catalysts such as Pd/Pb/Mg Al_2O_3 (e.g., as described in JP 2006306731) and $Pd_xBi_yFe/CaCO_3$ (Scheme 9.

SCHEME 9:



Additionally, all materials currently produced from butadiene such as synthetic rubbers and nylon can be manufactured from the renewable butadiene produced by the dehydrogenation of renewable butenes according to the present invention. For example, butadiene is used directly as a monomer and co-monomer for the production of synthetic rubber. It is also converted into "oxidized" monomers such as 1,4-butanediol, adiponitrile, and adipic acid as described herein for the production of polyester and nylon materials (e.g., adipic acid is produced by the hydrocarboxylation of butadiene in the presence of a suitable catalyst, CO and water; e.g., adiponitrile is produced by the hydrocyanation of butadiene in the presence of a suitable catalyst). The production of renewable isoprene from the dehydrogenation of methylbutenes or the hydroformylation and dehydration of renewable isobutene allows the preparation of renewable or partially renewable versions of all chemicals and materials produced from isoprene, especially synthetic rubber and other polymers.

One of the major industrial uses of isobutene is in the production of butyl rubber primarily for use in automobile tires. Butyl rubber is a high performance polymer comprised of high purity isobutene crosslinked with di-olefins such as butadiene or isoprene (e.g., U.S. Pat. No. 2,984,644; Dhaliwal G K, *Rubber Chemistry and Technology* 1994 (67) 567). Typically, 1-3% of di-olefin is blended with isobutene and co-polymerized in the presence of a polymerization catalyst such as aluminum chloride and other metal salts.

In some embodiments, renewable isoprene is produced by contacting 3-methyl-1-butanol or 2-methyl-1-butanol with a dehydration catalyst and a dehydrogenation catalyst, under conditions similar to those described herein for preparing renewable butadiene. The renewable isoprene thus formed may then blended with renewable isobutene, obtained by the methods described above or by conventional methods such as hydration of isobutylene to t-butanol and subsequent dehydration to isobutene, to form a renewable monomer feedstock for the production of renewable butyl rubber. Petroleum-based isoprene and isobutene can also used with the renewable isoprene and/or isobutene to produce butyl rubber that is partially renewable. In addition to blending purified isoprene with purified isobutene to produce butyl rubber, a renewable blend of isobutene and isoprene can be produced by contacting a mixture of isobutanol and 3-methyl-1-butanol (or 2-methyl-1-butanol) with a dehydration catalyst to form isobutylene and 3-methyl-butenes (or 2-methyl-butenes) and then contacting this olefin mixture with a dehydrogenation catalyst to form isobutene and isoprene. By-products such as butadiene and other C_5 olefins and di-olefins are removed by extractive distillation to give mixtures containing only isobutene and isoprene. The amount of isoprene in the mixture can be Controlled by manipulating the 3-methyl-1-butanol producing pathway in the host microorganism or the appropriate selection of catalyst in the thermochemical conversion of biomass. In some embodiments, the 3-methyl-1-butanol (or 2-methyl-1-butanol) concentration is tuned to 1-3% of the isobutanol produced such that the resulting isobutene/isoprene mixture can be directly used to produce butyl rubber. Alternatively, in other embodiments a higher concentration of 3-methyl-1-butanol is produced to form a mixture of isobutene and isoprene that is then diluted with pure isobutene to optimize butyl rubber production. The isoprene produced from 3-methyl-1-butanol (or 2-methyl-1-butanol) containing isobutanol is also separately removed and blended with isobutene to the appropriate concentration. Alternatively, the butadiene produced by the dehydrogenation of 1- and 2-butenes is used as a cross-linking agent in a butyl rubber product.

In view of the foregoing description, it will be appreciated that starting from simple renewable ethanol and isobutanol feedstocks, essentially any product currently derived or produced from petroleum feedstocks can be produced by the present integrated processes. Exemplary methods of producing certain renewable mono- and polyolefins, unsubstituted and substituted aromatics, derivatives thereof (e.g., acids, esters, acid derivatives, heterosubstituted compounds, etc.) and polymers and products therefrom have been described. It will be appreciated that methods and/or transformation as described herein for one compound are generally analogous and applicable to other, similar compounds and that such transformations and products are within the scope of the present integrated methods.

The present integrated processes will now be further described with reference to the following, non-limiting examples.

Example 1

Production of Isobutanol from Lignocellulosics

A cellulosic material consisting of 45% cellulose, 25% hemicellulose, 22% lignin and 8% other materials is pretreated to yield a slurry of 8% insoluble cellulose with about 4% insoluble lignin, 1% glucose, 40 g/L xylose, 2 g/L mannose, 2 g/L galactose, 1 g/L arabinose, 5 g/L acetic acid in

solution. The slurry is fed into an agitated saccharification and fermentation vessel and charged with cellulase enzyme sufficient to hydrolyze 80% of the cellulose 72 hours. A microorganism known to ferment glucose, xylose, mannose, galactose and arabinose to isobutanol is added to the fermentation, and the vessel is agitated for 72 hours. Isobutanol produced by the fermentation is separated from the fermentation broth by distillation. The first isobutanol-containing distillation cut contains 20% w/w isobutanol and 80% w/w water that condenses to form two phases—a light phase containing 85% isobutanol and 15% water and a heavy phase containing 8% isobutanol and 92% water. The light phase is distilled a second time and two low-water cuts of isobutanol are obtained. One cut is comprised of 99.5% isobutanol and 0.5% water while the second cut is comprised of 98.8% isobutanol, 1% 3-methyl-1-butanol, and 0.2% water.

Example 2

Dehydration of Isobutanol

Isobutanol obtained in Example 1 was fed through a preheater and to a fixed-bed tubular reactor packed with a commercial dehydration catalyst (BASF Al-3996). The internal reactor temperature was maintained at 300° C. and the reactor pressure was atmospheric. The WHSV of the isobutanol was 6 hr^{-1}. Primarily isobutene and water were produced in the reactor and separated in a gas-liquid separator at 20° C.; the water had 1% of unreacted isobutanol and conversion was 99.8%. GC-MS of the gas phase effluent indicated it was 96% isobutene, 2.5% 2-butene (cis and trans) and 1.5% 1-butene.

Example 3

Dehydration of Isobutanol

Isobutanol obtained in Example 1 is fed through a preheater and to a fixed-bed tubular reactor packed with a commercial dehydration catalyst (e.g., an X-type zeolite). The internal reactor temperature is maintained at 370° C. and the reactor pressure is atmospheric. The WHSV of the isobutanol is 3 hr^{-1}. A mixture of C_4 olefins and water are produced in the reactor and separated in a gas-liquid separator at 20° C.; the water has ≤1% of unreacted isobutanol and conversion is ≥99.8%. GC-MS of the gas phase effluent indicates it is 50% isobutene, 40% 2-butene (cis and trans) and 10% 1-butene.

Example 4

Co-Dehydration of Ethanol and Isobutanol

60 g of a commercial γ-alumina dehydration catalyst (BASF Al-3996) is loaded into a fixed-bed tubular reactor. A feed mixture is prepared by mixing 250 mL of ethanol with 750 mL of isobutanol. The feed mixture is pumped through a preheater and onto the catalyst bed at a feed rate of 2.5 mL/min. The internal reactor temperature is maintained at 350° C., the pressure was atmospheric, and the weight hourly space velocity (WHSV) of the mixed alcohol feed is ~2/hr. The products are separated in a gas-liquid separator. The water contains 0.9 wt % ethanol and 0.3 wt % isobutanol indicating conversions of 99% and 99.9% respectively. The gas-phase effluent is 35% ethylene and 65% butenes (molar basis). The butenes are found to be 55% isobutene, 13% 1-butene, 12% cis-2-butene, and 20% trans-2-butene.

Example 4A

Dehydration of Dry Isobutanol

Dry isobutanol (<1 wt % water) obtained in Example 1 was fed through a preheater to a fixed-bed tubular reactor packed with a commercial γ-alumina dehydration catalyst (BASF Al-3996). The internal reactor temperature was maintained at 325° C. and the reactor pressure was atmospheric. The WHSV of the isobutanol was 5 hr^{-1}. Primarily isobutene and water were produced in the reactor, and were separated in a gas-liquid separator at 20° C.; the water had <1% of unreacted isobutanol and the conversion was >99.8%. GC-FID analysis of the gas phase effluent indicated it was 95% isobutene, 3.5% 2-butene (cis and trans) and 1.5% 1-butene.

Example 5

Purification of Isobutene by Dehydrogenation of Butenes

A mixed butene stream from Example 2, containing 96% isobutene, 2.5% 2-butenes (cis and trans), and 1.5% 1-butene is mixed with air at a relative feed rate of 10:1 butenes:air. The resultant mixture is 1.9% oxygen and 3.6% linear butenes. The mixture is preheated to 400° C. and fed at a GHSV of 300 hr^{-1} to a fixed-bed tubular reactor loaded with 2 catalyst beds in sequence: the first contains $ZnFe_2O_4$ and the second contains $Co_6Fe_2BiMoO_5$. The effluent from the reactor is dried over a molecular sieve column to remove water. Nitrogen and oxygen are removed by passing the C_4 stream through a gas-liquid separator at −78° C. (dry ice bath). The C_4 product is analyzed via GC-MS. The composition is found to be 96% isobutene, 3.9% butadiene, and 0.1% linear butenes. butadiene is stripped from the gas stream by extraction with acetonitrile. The resultant stream is 99.9% isobutene and 0.1% linear butenes with trace butadiene (<0.01%).

Example 6

Purification of Isobutene by Dehydrogenation of Butenes

A mixed butene stream from Example 3, containing 50% isobutene, 40% 2-butenes (cis and trans), and 10% 1-butene is mixed with air at a relative feed rate of 4:5 butenes:air. The resultant mixture is 11.7% oxygen and 22.2% linear butenes. The mixture is preheated to 400° C. and fed at a GHSV of 300 hr^{-1} to a fixed-bed tubular reactor loaded with 2 catalyst beds in sequence: the first contains $ZnFe_2O_4$ and the second contains $Co_6Fe_2BiMoO_5$. The effluent from the reactor is dried over a molecular sieve column to remove water. Nitrogen and oxygen are removed by passing the C_4 stream through a gas-liquid separator at −78° C. (dry ice bath). The C_4 product is analyzed via GC-MS. The composition is found to be 50% isobutene, 49.9% butadiene, and 0.1% linear butenes. butadiene is stripped from the gas stream by extraction with acetonitrile. The resultant stream is 99.9% isobutene and 0.1% linear butenes with trace butadiene (<0.01%).

Example 7

Preparation of Butadiene from Butenes

120 sccm of nitrogen and 120 sccm of 2-butene (mixture of cis and trans) was fed through a preheater and to a fixed-bed tubular reactor packed with 15 g of a commercial Cr_2O_3 on

alumina dehydrogenation catalyst (BASF Snap catalyst). The internal reactor temperature was maintained at 600° C. and the reactor pressure was atmospheric. The WHSV of the 2-butene was about 1 hr^{-1}. GC-FID of the gas phase effluent indicated it was 74% linear butenes (mixture of 1-, cis-2-, and trans-2-), 16% butadiene, 2.5% n-butane, and 7.5% C_1-C_3 hydrocarbons. The resulting conversion of 2-butene was 26% (ignoring rearrangement to 1-butene) with a selectivity to butadiene of 61.5% based on % carbon.

Example 9

Integrated Preparation of Butadiene from Isobutanol

Renewable wet isobutanol (containing 15% water and ~4% ethanol) obtained from fermentation was fed through a preheater and to a fixed-bed tubular reactor packed with a commercial γ-alumina dehydration catalyst (BASF Snap catalyst). The internal reactor temperature was maintained at 400° C. and the reactor pressure was atmospheric. The WHSV of the isobutanol was ~0.1 hr^{-1}. The products were separated in a gas-liquid separator at 20° C., where relatively pure water was removed as the liquid product. The gas phase product was dried over a molecular sieve bed. GC-FID of the gas phase effluent from the dehydration reactor was 82% isobutylene, 13% linear butenes (mixture of 1-butene, and cis- and trans-2-butene), 4.5% ethylene, and 0.5% propylene. The flow of the gas-phase stream was ~120 sccm. This stream was combined with 120 sccm of nitrogen and was fed through a preheater and to a fixed-bed tubular reactor packed with 15 g of a commercial Cr_2O_3 on alumina dehydrogenation catalyst. The internal reactor temperature was maintained at 600° C. and the reactor pressure was atmospheric. The WHSV of the mixed butene stream was about 1 hr^{-1}. GC-FID of the gas phase effluent indicated it was 78.5% isobutylene with 2.5% isobutane, 7.5% linear butenes, 3.7% ethylene with 0.6% ethane, 2.9% butadiene, and the remaining 4.4% was methane and propylene. This indicates an approximate yield of 22% butadiene based on linear butenes fed to the dehydrogenation reactor.

Example 10

Preparation of Propylene from Ethylene and 2-Butenes

A metathesis catalyst is prepared by dissolving 0.83 g of ammonium metatungstate in 100 mL of distilled water, stirring the resulting solution with 5 g of silica gel (300 m^2/g, pore volume 1 mL/g), evaporating the water, then calcining the resulting solid in air at 550° C. for 6 hours. The resulting supported tungsten oxide catalyst is then mixed with hydrotalcite at a weight ratio of about 1:5 tungsten oxide catalyst/hydrotalcite. A metathesis reactor is then prepared by adding the tungsten oxide catalyst/hydrotalcite catalyst to a fixed-bed tubular reactor.

An ethylene guard column is prepared by loading a fixed-bed tubular reactor sequentially with approximately equal amounts of hydrotalcite and γ-alumina, and a butene guard column is prepared by loading a fixed-bed tubular reactor sequentially with the tungsten oxide catalyst (prepared as described above) and approximately twice the amount (by weight) of hydrotalcite.

The disproportionation reaction is carried out by first purging the guard columns and metathesis reactor with an approximately 100 mL/min flow of N2 at atmospheric pressure. The purged reactor and guard columns are then heated to 500° C. with continuing N2 flow for 1 hr. The guard columns and reactors are maintained at 500° C.; then approximately 100 mL/min of H2 gas at atmospheric pressure is added to the N2 purge, and maintained for 2 hrs. The reactor is then cooled to 200° C., and the guard columns cooled to 50° C., and the flow of N2 and H2 is reduced to 50 mL/min. After purification in the respective guard columns, liquefied renewable 2-butene is then introduced into the butene guard column at a rate of 0.10 g/min, and liquefied renewable ethylene is introduced into the ethylene guard column at a flow rate of 64.5 mL/min and a pressure of 3.5 MPa. The ethylene, 2-butene, and H2 (7.0 mL/min, 3.5 MPa) were then charged into the metathesis reactor (after preheating to 200° C.). The butene conversion rate obtained by subtracting the total amount of trans-2-butene, cis-2-butene and 1-butene contained in the outlet gas from the metathesis reactor is 71%. The propylene selectivity based on butene is 90%. Small amounts of propane, pentene and hexene are also produced.

Example 11

Oligomerization of Isobutene

The product stream from Example 4a was dried over molecular sieves, compressed to 60 psig, cooled to 20° C. so that the isobutene was condensed to a liquid and pumped with a positive displacement pump into a fixed-bed oligomerization reactor packed with a commercial ZSM-5 catalyst (CBV 2314). The reactor was maintained at 175° C. and a pressure of 750 psig. The WHSV of the isobutene-rich stream was 15 hr^{-1}. The reactor effluent stream was 10% unreacted butenes, 60% isooctenes (primarily 2,4,4-trimethylpentenes), 28% trimers, and 2% tetramers.

Example 12

Oligomerization of Isobutene

The product stream from Example 4a is co-fed with 50% isobutane to a compressor, condensed and pumped into a fixed-bed oligomerization reactor packed with Amberlyst 35 (strongly acidic ionic exchange resin available from Rohm & Haas). The reactor is maintained at 120° C. and a pressure of 500 psig. The WHSV of the isobutene-rich stream is 100 hr^{-1}. The product stream is about 50% isobutane (diluents), about 3% unreacted butenes, about 44% isooctenes (primarily 2,4,4-trimethylpentenes), and about 3% trimers.

Example 13

Dehydrocyclization of Isooctene

Isooctene from Example 11 was distilled to remove trimers and tetramers and then fed at a molar ratio of 1.3:1 mol nitrogen diluent gas to a fixed bed reactor containing a commercial chromium oxide doped alumina catalyst (BASF D-11451E ⅛"). The reaction was carried out at atmospheric pressure and a temperature of 550° C., with a WHSV of 1.1 hr^{-1}. The reactor product was condensed and analyzed by GC-MS. Of the xylene fraction, p-xylene was produced in greater than 80% selectivity. Analysis by method ASTM D6866-08 showed p-xylene to contain 96% biobased material.

Example 14

Hydrogenation of Isooctene

Palladium on carbon (0.5% Pd/C, 2 g) catalyst was charged into a 2000 mL stainless steel batch reactor equipped with

stirrer. 1000 mL of a hydrocarbon fraction comprising isooctene isomers was charged into the reactor. The reactor was then flushed with nitrogen and pressurized with 100 psig hydrogen. The reaction mixture was stirred for one hour and the temperature was increased from ambient temperature to 80-100° C. The reactor was subsequently cooled down to ambient temperature and excess hydrogen remaining in the reactor was released. and the reactor purged with a small amount of nitrogen. The product was filtered off from the catalyst and GC analysis of the product showed 100% hydrogenation.

Example 15

Oxidation of Renewable P-Xylene to Terephthalic Acid

A 300 mL Pan reactor was charged with glacial acetic acid, bromoacetic acid. cobalt acetate tetrahydrate. and p-xylene. obtained from Example 13. in a 1:0.01:0.025:0.03 mol ratio of glacial acetic acid:bromoacetic acid: cobalt acetate tetrahydrate: p-xylene. The reactor was equipped with a thermocouple. mechanical stirrer, oxygen inlet, condenser, pressure gauge. and pressure relief valve. The reactor was sealed and heated to 150° C. The contents were stirred and oxygen was bubbled through the solution. A Pressure of 50-60 psi was maintained in the system and these reaction conditions were maintained for 4 h. After 4 h. the reactor was cooled to room temperature. Terephthalic acid was filtered from solution and washed with fresh glacial acetic acid.

Example 16

Purification of Renewable Terephthalic Acid

Terephthalic acid from Example 15 was charged to a 300 mL Pan reactor with 10% Pd on carbon catalyst in a 4.5:1 mol ratio of terephthalic acid:10% Pd on carbon. Deionized water was charged to the reactor to make a slurry containing 13.5 wt. % terephthalic acid. The reactor was equipped with a thermocouple. mechanical stirrer, nitrogen inlet, hydrogen inlet, pressure gauge, and pressure relief valve. The Parr reactor was sealed and flushed with nitrogen. The Parr reactor was then filled with hydrogen until the pressure inside the reactor reached 600 psi. The reactor was heated to 285° C. and the pressure inside the vessel reached 1000 psi. The contents were stirred under these conditions for 6 h. After 6 h. contents were cooled to room temperature and filtered. The residue was transferred to a vial and N,N-dimethylacetamide was added to the vial in a 5:1 mol ratio of N,N-dimethylacetamide:terephthalic acid. The vial was warmed to 80° C. for 30 minutes to dissolve the terephthalic acid. The contents were filtered immediately: Pd on carbon was effectively removed from the terephthalic acid. Crystallized terephthalic acid filtrate was removed from the collection flask and was transferred to a clean filter where it was washed with fresh N,N-dimethylacetamide and dried. A yield of 60% purified terephthalic acid was obtained.

Example 17

Polymerization of Terephthalic Acid to Make Renewable Pet

Purified terephthalic acid (PTA) obtained from Example 16 and ethylene glycol are charged to a 300 mL Parr reactor in a 1:0.9 mol ratio of PTA:ethylene glycol. Antimony (III) oxide is charged to the reactor in a 1:0.00015 mol ratio of PTA:antimony (III) oxide. The reactor is equipped with a thermocouple, mechanical stirrer, nitrogen inlet, vacuum inlet, condenser. pressure gauge. and pressure relief valve. The Parr reactor is sealed. flushed with nitrogen. heated to a temperature of 240° C., and pressurized to 4.5 bar with nitrogen. Contents are stirred under these conditions for 3 h. After 3 h. the temperature is increased to 280° C. and the system pressure is reduced to 20-30 mm by connecting the reactor to a vacuum pump. Contents are stirred under these conditions for 3 h. After 3 h. the vacuum valve is closed and the contents of the reactor are flushed with nitrogen. The reactor is opened and contents are immediately poured into cold water to form PET pellets.

Example 18

Preparation of Diisobutylene from Isobutanol

Isobutanol produced by fermentation was separated from the fermentation broth by distillation. The isobutanol. which contains 16% water, was passed through a chemical reactor containing a commercial γ-alumina catalyst heated to 310° C. at ~10 psig and a WHSV of 6 hr^{-1}. The water drained from the bottom of the reactor contained less than 0.1 M isobutanol. and isobutylene (gas) was collected with >99% conversion. The isobutylene gas was dried by passing it through molecular sieves, and was then fed into a second reactor containing a ZSM-5 catalyst maintained at 140-160° C., ambient pressure. and WHSV 1.5 hr^{-1} to give ~60% conversion to a mixture of about 80% of diisobutylene isomers and about 20% triisobutylene isomers and minor quantities of higher molecular weight products.

Example 19

Preparation of Isododecane from Isobutanol

Isobutanol produced by fermentation (e.g. according to Example 1) was separated from the fermentation broth by distillation. The isobutanol. which contains 16% water. was passed through a chemical reactor containing acidic commercial γ-alumina catalyst heated to 310° C. at ~10 psig and a WHSV of 6 hr^{-1}. The water drained from the bottom of the reactor contained less than 0.1 M isobutanol. and isobutylene (gas) was collected with >99% conversion. The isobutylene gas was dried by passing it through molecular sieves. and was then fed into a second reactor containing Amberlyst® 35. maintained at 100-120° C., ambient pressure. and WHSV 2.5 hr^{-1} to give ~90% conversion to a mixture of about 15% of diisobutylene isomers, 75% triisobutylene isomers and 10% tetramers. The liquid product was pumped to a trickle-bed hydrogenation reactor packed with a commercial 0.5% Pd on alumina catalyst and co-fed with 10% excess hydrogen. Hydrogenation of >99% of the olefins occurred at 150° C., 150 psig. and WHSV 3 hr^{-1}. The saturated hydrocarbon product was collected with an overall process yield of ~90%.

Example 20

Preparation of Gasoline from Dimers and Trimers of Isobutylene

A mixture of about 80% diisobutylene isomers and about 20% triisobutylene isomers and minor quantities of higher molecular weight products was fed into a hydrogenation reac-

tor containing a 0.5% Pd on alumina catalyst maintained at 150° C. and 150 psi to give a saturated hydrocarbon product, which was distilled at atmospheric pressure to give three fractions containing diisobutylene, triisobutylene and small quantities of higher molecular weight products. The three fractions can be separated and used in aviation gasoline and auto gasoline.

Example 21

Preparation of Methylundecene from Isobutylene

90 g of renewable isobutylene was loaded into a 350 mL batch reactor with 10 g of a ZSM-5 catalyst (Si:Al ratio 80) that had been treated with 2,4,6-trimethyl pyridine. The sealed reactor was heated to 220° C. and allowed to react for approximately 40 hours. 75 mL of product was collected and a sample was analyzed by GC/MS. The composition was approximately 30% C_{12} or larger molecules and the primary compounds were isomers of methylundecene.

Example 22

Preparation of Diesel Fuel from Methylundecene

The unsaturated product from Example 21 was loaded into a 350 mL batch reactor containing 1 g of 5% Pd/C catalyst. The reactor was flushed with nitrogen and pressurized with 200 psig of hydrogen. The reactor was heated to 100° C. and held at this temperature for 1 hour. 70 mL of product was collected and analyzed by GC/MS. The product was found to be fully saturated. 70 mL of this hydrogenated mixture was then distilled to concentrate the C_{12}+ fraction (e.g., the fraction containing C_{12} or higher hydrocarbons). Approximately 50 mL of the mixture was distilled off (primarily C_8 hydrocarbons), leaving 20 mL of C_{12}+ hydrocarbons. The flash point of the final product was measured as 51° C. and the derived cetane number was measured by ASTM D6890-07 as 68. The product was determined to meet the ASTM specifications for #1 diesel fuel.

Example 23

Jet Fuel from Isobutylene

Renewable isobutylene was trimerized using a fixed bed continuous flow system equipped with a tube furnace housing SS 316 reactor (OD ⅜ inx12 in), gas flow meters, an HPLC pump, a back pressure regulator, and a gas-liquid separator. In a typical trimerization procedure, the reactor was loaded with β Zeolite CP 814C (Zeolyst International) and isobutylene was fed at WHSV 1-3 hr^{-1} at a reaction temperature of 140-180° C., at atmospheric pressure. The isobutylene conversion was 85% with a product distribution of about 29% dimer isomers, 58% trimer isomers, and 11% tetramer isomers. The hydrogenation of the resulting oligomer blend was carried out at 150° C. and 150 psi H_2 to give a hydrocarbon product which was fractionated to provide a blend of saturated C_{12} (trimers) and C_{16} (tetramers) hydrocarbons that were used as a jet fuel feedstock.

Example 24

Preparation of BTEX from Isobutylene

A fixed bed continuous flow system equipped with a tube furnace housing SS 316 reactor (OD ⅜ inx12 in), gas flow meters, an HPLC pump, back pressure regulator, and a gas-liquid separator was loaded with ZSM-5 CBV 8014 Zeolite catalyst. The catalyst was calcined at 540° C. under N_2 for 8 hrs before the reaction was started. Isobutylene (e.g., prepared as described herein) was fed into the reactor at WHSV 1.0 hr^{-1} and the reaction conditions were maintained at 400-550° C. and atmospheric pressure. Aromatic products were formed in about 45% yield and the selectivity for BTEX (e.g., benzene, toluene, ethylbenzene and xylene) was 80%. The aromatic product was separated and used in fuels and other products.

Example 25

Preparation of BTEX and Hydrogen from Diisobutylene

A fixed bed continuous flow reactor was loaded with ZSM-5 CBV 8014 Zeolite catalyst. Prior to initiating the reaction, the catalyst was calcined at 540° C. under N_2 for 8 hrs. Isobutylene was fed into the reactor at a WHSV of 1.6 h^{-1} while the reaction conditions were maintained at 400-550° C. and atmospheric pressure. Aromatic products were formed in about 38% yield and with a selectivity for BTEX of 80%. The aromatic products were isolated and used in fuels and other products. Hydrogen also was produced as a byproduct of the reaction: about 3 moles of hydrogen were produced for each mole of aromatic ring formed.

Example 26

Integrated Oligomers Production from Isobutylene

Isobutanol produced by fermentation (e.g., as described herein) was separated from the fermentation broth by distillation. The isobutanol, which contains 16% water, was passed through a chemical reactor containing pelleted SPA catalyst heated to 350° C. at 1 atmosphere. Water was drained from the bottom of the reactor and isobutylene was collected with 99% conversion. The isobutylene gas was dried by passing it through molecular sieves, and was then fed into a second reactor containing Amberlyst® 35 (Rohm and Haas) catalyst maintained at 120-140° C. and ambient pressure to give 90% conversion to a mixture of about 27% of diisobutylene isomers and about 70% triisobutylene isomers, and minor quantities of higher molecular weight products.

Example 27

Integrated Saturated Oligomers Production from Isobutylene

Isobutanol produced by fermentation (e.g., as described herein) was separated from the fermentation broth by distillation. The isobutanol, which contains 16% water, was passed through a chemical reactor containing pelleted SPA catalyst heated to 350° C. at 1 atmosphere. Water was drained from the bottom of the reactor and isobutylene was collected with 99% conversion. The isobutylene gas was dried by passing it through molecular sieves, and then fed into a second reactor containing Amberlyst® 35 (Rohm and Haas) catalyst maintained at 120-140° C. and ambient pressure to give 90% conversion to a mixture of about 27% of diisobutylene isomers and about 70% triisobutylene isomers and minor quantities of higher molecular weight products. This oligomers blend was then fed into a third reactor to hydrogenate the olefins over 0.5% Pd supported in alumina at 150° C. and 150

psi H_2. The resulting product was fractionated to isolate a blend of isobutylene trimers and tetramers that were used as a jet fuel feedstock.

Example 28

Integrated Production of P-Xylene from Isobutanol

Renewable isobutanol is converted to renewable p-xylene using a process illustrated in FIG. **10**. Renewable isobutanol (e.g., as described herein) is fed wet (15 wt % water) through a preheater into a fixed-bed catalyst reactor packed with a commercial γ-alumina catalyst (BASF AL-3996) at a WHSV of 10 hr^{-1}. The dehydration reactor is maintained at 290° C. at a pressure of 60 psig. The effluent (3) from the dehydration reactor is fed to a liquid/liquid separator, where water is removed. Analysis of the organic phase (4) shows that it is 95% isobutylene, 3% linear butenes, and 2% unreacted isobutanol. The organic phase is combined with a recycle stream (11) containing isobutane, isooctane, and unreacted butenes and fed to a positive displacement pump (P2) where it is pumped to an oligomerization reactor packed with HZSM-5 catalyst (CBV 2314) at a WHSV of 100 hr^{-1}. The reactor is maintained at 170° C. at a pressure of 750 psig. The effluent (6) from the oligomerization reactor is analyzed and shown to contain 60% unreacted feed (isobutane, isooctane, and butenes), 39% isooctene, and 1% trimers. The effluent from the oligomerization reactor is combined with recycled isooctene (15) and fed through a preheater and to a fixed bed reactor containing a commercial chromium oxide doped alumina catalyst (BASF D-11451 ⅛") at a WHSV of 1 hr^{-1}. The dehydrocyclization reactor is maintained at 550° C. and 5 psia. The yield of xylenes from the reactor relative to C_8 alkenes in the feed is 42% with a selectivity to p-xylene of 90%. The effluent (8) is separated with a gas-liquid separator. The gas-phase is compressed (C1) to 60 psig causing the isobutane and butenes to condense. A second gas-liquid separator is used to recover the hydrogen (and small quantities of methane or other light hydrocarbons). The C_4 liquids are recycled (11) and combined with the organic phase from the dehydration reactor (4). The liquid product (12) from the dehydrocyclization reactor is fed to a series of distillation columns slightly above atmospheric pressure by a pump (P3). Any by-product light aromatics (benzene and toluene) and heavy compounds (C_9+ aromatics or isoolefins) are removed. A side stream (14) rich in xylenes and iso-C_8 compounds are fed to a second distillation column. The C8 compounds (isooctene and isooctane) are recycled (15) to the feed of the dehydrocyclization reactor. The xylene fraction (16) is fed to a purification process resulting in a 99.99% pure p-xylene product and a small byproduct stream rich in o-xylene.

The embodiments described herein and illustrated by the foregoing examples should be understood to be illustrative of the present invention, and should not be construed as limiting. On the contrary, the present disclosure embraces alternatives and equivalents thereof, as embodied by the appended claims.

We claim:

1. An integrated process for preparing renewable hydrocarbons, comprising:

(a) providing renewable isobutanol and renewable ethanol;

(b) dehydrating the renewable isobutanol, thereby forming a renewable butene mixture comprising one or more renewable linear butenes and renewable isobutene;

(c) dehydrating the renewable ethanol, thereby forming renewable ethylene;

(d) reacting at least a portion of the renewable butene mixture and at least a portion of the renewable ethylene to form one or more renewable C_3-C_{16} olefins;

(e) forming renewable hydrogen by one or more of:

(e1) isolating and dehydrogenating at least a portion of the linear butenes formed in step (b) and/or one or more renewable C_4-C_{16} olefins formed in step (d) thereby forming one or more renewable C_4-C_{16} dienes and renewable hydrogen;

(e2) isolating and dehydrocyclizing at least a portion of one or more renewable C_6-C_{16} olefins formed in step (d), thereby forming one or more renewable C_6-C_{16} aromatics and renewable hydrogen;

(e3) isolating and dehydrocyclizing at least a portion of one or more renewable C_6-C_{16} dienes formed in step (e1) to form one or more renewable C_6-C_{16} aromatics and renewable hydrogen; and

(f) hydrogenating at least a portion of the renewable C_3-C_{16} olefins with the renewable hydrogen formed in step (e), thereby forming a renewable saturated hydrocarbon fuel or fuel additive, wherein the amount of said dehydrogenating and/or dehydrocyclizing in step (e), and/or the amount of hydrogenating in step (f) are controlled so that the amount of renewable hydrogen formed in step (e) is essentially completely consumed in step (f).

2. The integrated process of claim **1**, wherein the one or more renewable linear butenes comprise 2-butene.

3. The integrated process of claim **1**, wherein said reacting of step (d) comprises one or more reactions selected from the group consisting of disproportionation, metathesis, oligomerization, isomerization, alkylation, dehydrodimerization, dehydrocyclization, and combinations thereof.

4. The integrated process of claim **1**, wherein said reacting of step (d) comprises dimerizing at least a portion of the renewable isobutene, thereby forming a renewable isobutene dimer mixture comprising at least one C_8 hydrocarbon selected from the group consisting of a 2,4,4-trimethylpentene, a 2,5-dimethylhexene, and 2,5-dimethylhexadienes, and combinations thereof.

5. The integrated process of claim **1**, wherein said reacting of step (d) comprises trimerizing at least a portion of the renewable isobutene, thereby forming a renewable isobutene trimer mixture comprising 2,2,4,6,6-pentamethylheptene.

6. The integrated process of claim **1**, wherein said reacting of step (d) comprises tetramerizing at least a portion of the renewable isobutene, thereby forming a renewable isobutene tetramer mixture, wherein the renewable isobutene tetramer mixture comprises 2,2,4,6,6,8,8-heptamethylnonene.

7. The integrated process of claim **1**, wherein said reacting of step (d) comprises isomerizing at least a portion of the renewable isobutene of step (b) to form an isobutene isomerization mixture comprising renewable 2-butene, wherein said reacting of step (d) further comprises disproportionating at least a portion of the renewable ethylene formed in step (c) and at least a portion of the renewable 2-butene formed by isomerizing at least a portion of the renewable isobutene of step (b), thereby forming renewable propylene.

8. The integrated process of claim **2**, wherein said reacting of step (d) comprises disproportionating at least a portion of the renewable ethylene formed in step (c) and at least a portion of the renewable 2-butene formed in step (b), thereby forming renewable propylene.

9. The integrated process of claim **2**, wherein said reacting of step (d) comprises disproportionating at least a portion of the renewable ethylene formed in step (c), and at least a portion of the renewable 2-butene formed in step (b) and

renewable 2-butene formed by isomerizing the renewable isobutene formed in step (b), thereby forming renewable propylene.

10. The integrated process of claim **1**, wherein step (e) comprises step (e1).

11. The integrated process of claim **10**, wherein the one or more renewable C_4-C_{15} dienes formed in step (e1) comprise butadiene.

12. The integrated process of claim **1**, wherein step (e) comprises step (e2).

13. The integrated process of claim **12**, wherein the one or more renewable C_6-C_{16} aromatics formed in step (e2) comprise renewable p-xylene.

14. The integrated process of claim **1**, wherein step (e) comprises step (e1) and step (e2).

15. The integrated process of claim **1**, wherein step (e) comprises step (e1) and step (e3).

16. The integrated process of claim **1**, wherein step (e) comprises step (e1), step (e2), and step (e3).

17. The integrated process of claim **4**, wherein at least a portion of the renewable isobutene dimer mixture is hydrogenated in step (f), whereby the renewable saturated hydrocarbon fuel or fuel additive comprises isooctane, wherein the renewable isobutene dimer mixture is hydrogenated in step (f), whereby the renewable saturated hydrocarbon fuel or fuel additive comprises isooctane.

18. The integrated process of claim **5**, wherein at least a portion of the renewable isobutene trimer mixture is hydrogenated in step (f), whereby the renewable saturated hydrocarbon fuel or fuel additive comprises one or more pentamethylheptanes, wherein the renewable isobutene trimer mixture is hydrogenated in step (f), whereby the renewable saturated hydrocarbon fuel or fuel additive comprises one or more pentamethylheptanes.

19. The integrated process of claim **1**, wherein said reacting of step (d) further comprises mixing said renewable butene mixture and/or said renewable ethylene with at least a portion of a non-renewable butene and/or a butene mixture and/or non-renewable renewable ethylene to form one or more C_3-C_{16} olefins, and at least a portion of said one or more C_3-C_{16} olefins are renewable.

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(54) **NATURAL ANTIMICROBIAL COMPOSITIONS**

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(57) **ABSTRACT**

The present invention provides novel antimicrobial compositions. In one embodiment, the antimicrobial composition comprises an antimicrobial effective amount of a mixture comprising (a) two or more fatty acids, each of which is natural or naturally derived, and (b) at least one of (i) a natural or naturally derived product, (ii) an alcoholic solvent, or (iii) an organic acid or a salt thereof. The present invention also provides a product comprising a preservative effective amount of the aforementioned mixture.

NATURAL ANTIMICROBIAL COMPOSITIONS

[0001] The present application claims the benefit of U.S. Provisional Application No. 61/482,353, filed May 4, 2011, which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to antimicrobial mixtures, for instance, comprising (a) two or more fatty acids, each of which is natural or naturally derived, and (b) at least one of (i) a natural or naturally derived product, (ii) an alcoholic solvent, or (iii) an organic acid.

BACKGROUND

[0003] There are many drawbacks to currently available natural and naturally-derived antimicrobial formulations. They are expensive, and high concentrations of them (for instance, >2%) are often required to prevent microbial growth and preserve a product. Many have undesirable colors and odors, have poor stability (for example, in aqueous systems), and are not effective against a broad spectrum of microorganisms. Additionally, some such natural or naturally-derived antimicrobial mixtures cause thinning of formulations. Many are oils or extracts which limits their usage in various formulations.

[0004] There is a continuing need for low cost and safe natural preservative systems which are effective against a broad spectrum of microorganisms.

SUMMARY OF THE INVENTION

[0005] The antimicrobial compositions of the present invention are relatively cheap to make, easy to work with and incorporate into finished products, generally have no odor, and have reduced (compared to prior oil preservative systems) or no color.

[0006] One embodiment of the present invention is an antimicrobial composition comprising an antimicrobial effective amount (such as a preservative, bactericidal, and/or fungicidal effective amount) of a mixture comprising:

[0007] (a) (i) two or more fatty acids, each of which is natural or naturally derived, or

[0008] (ii) a fatty acid and anisic acid, each of which is natural or naturally derived; and

[0009] (b) at least one of

[0010] (i) a natural or naturally derived product,

[0011] (ii) an alcoholic solvent, or

[0012] (iii) an organic acid or a salt thereof.

[0013] Preferred mixtures of the present invention include, but are not limited to, those shown in the table below.

Mixture No.	Component (a)	Component (b)
1	Caprylic acid and Lauric acid	1,3-Propanediol, and Potassium Sorbate
2	Caprylic acid and Lauric acid	1,3-Propanediol
3	Caprylic acid and Lauric acid	Glycereth-2 cocoate and Lauric acid
4	Caprylic acid and Lauric acid	1,3-Propanediol, and Benzoic acid
5	Caprylic acid and Lauric acid	Glycereth-2 cocoate

[0014] The present inventor has discovered that the combination of (a) lauric acid, (b) caprylic acid, and (c) glycereth-2 cocoate or 1,3-propanediol acts synergistically against bacteria and fungi, is readily soluble in aqueous systems, can readily solubilize waxy fatty acids, and forms a stable concentrate. The inventor has also discovered that caprylic acid solubilizes lauric acid to form a stable antimicrobial mixture. Lauric acid is generally not soluble in aqueous solutions.

[0015] Another embodiment is an antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

[0016] (a) caprylic acid (preferably natural or naturally derived).

[0017] (b) at least one waxy fatty acid, each of which is natural or naturally derived, and

[0018] (c) at least one of

[0019] (i) a natural or naturally derived product,

[0020] (ii) an alcoholic solvent, or

[0021] (iii) an organic acid.

[0022] In one embodiment, this mixture is present at a concentration of from about 0.01 to about 2% by weight, based on 100% total weight of the composition.

[0023] Yet another embodiment is an antimicrobial composition consisting essentially of an antimicrobial effective amount of a mixture consisting essentially of two or more fatty acids, each of which is natural or naturally derived. Suitable natural or naturally derived fatty acids include, but are not limited to, caprylhydroxamic acid, lauric acid, caprylic acid, capric acid, palmitic acid, and any combination of any of the foregoing. A preferred mixture consists essentially of caprylic acid and lauric acid. In a more preferred embodiment, the mixture consists essentially of at least about 50% by weight of caprylic acid, based upon 100% total weight of the antimicrobial mixture.

[0024] Yet another embodiment is an antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

[0025] (a) caprylic acid, which is natural or naturally derived.

[0026] (b) a natural or naturally derived product,

[0027] (c) an alcoholic solvent (for example, natural benzyl alcohol), and

[0028] (d) optionally, an organic acid or a salt thereof.

In one preferred embodiment, the mixture comprises caprylic acid, glycereth-2 cocoate, and ethylhexyl glycerin.

[0029] Yet another embodiment is an antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

[0030] (a) 1,3-propanediol (natural or naturally-derived),

[0031] (b) an alcoholic solvent (e.g., ethylhexyl glycerin), and

[0032] (c) optionally, an organic acid or a salt thereof (e.g., sorbic acid or a salt thereof).

In one preferred embodiment, the mixture comprises 1,3-propanediol (natural or naturally-derived), ethylhexyl glycerin, and potassium sorbate.

[0033] Preferred mixtures of the invention include, but are not limited to, those shown in the table below.

Mixture No.	Component (a)	Component (b)	Component (c)
6	1,3-Propanediol (natural or naturally derived)	Ethylhexyl glycerin	Potassium sorbate
7	1,3-Propanediol (natural or naturally derived)	Benzyl alcohol (preferably natural benzyl alcohol)	Benzoic acid
8	1,3-Propanediol (natural or naturally derived)	Ethylhexyl glycerin	Benzoic acid
9	1,3-Propanediol (natural or naturally derived)	Benzyl alcohol (preferably natural benzyl alcohol)	Caprylhydroxamic acid
10	1,3-Propanediol (natural or naturally derived)	Benzyl alcohol (preferably natural benzyl alcohol)	

[0034] One more preferred mixture comprises about 83% by weight of 1,3-propanediol (natural or naturally-derived), about 10% ethylhexyl glycerin, and about 7% potassium sorbate.

[0035] Preferably the mixtures of the present invention include an antimicrobial (e.g., preservative, bactericidal, and/or fungicidal) synergistic effective amount of the aforementioned ingredients. The antimicrobial composition is preferably substantially free or completely free of parabens (such as methylparaben, ethylparaben, and propylparaben). According to one embodiment, the antimicrobial composition contains less than about 2, 1.5, 1, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, or 0.01% by weight of parabens, formaldehyde donors, and/or isothiazolinones, based upon 100% total weight of antimicrobial composition. In another embodiment, the antimicrobial composition is substantially free or completely free of synthetic preservatives. According to one embodiment, the antimicrobial composition contains less than about 2, 1.5, 1, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, or 0.01% by weight of synthetic preservatives, based upon 100% total weight of antimicrobial composition.

[0036] Preferred mixtures of the present invention include, but are not limited to, those shown in the table below.

Mixture No.	Component (a)	Component (b)
1	about 45% caprylic acid + about 20% lauric acid	about 35% 1,3-propanediol + about 10% potassium sorbate
2	about 30% caprylic acid + about 25% lauric acid	about 35% 1,3-propanediol
3	about 60% caprylic acid	about 30% glycereth-2 cocoate + about 10% ethylhexyl glycerin (SEIG)
4	about 40% caprylic acid + about 20% lauric acid	about 35% glycereth-2 cocoate + about 20% lauric acid
5	about 70% caprylic acid	about 30% lauric acid
6	about 80% 1,3-propanediol	about 10% ethylhexyl glycerin + about 10% potassium sorbate
7	about 45% caprylic acid + about 20% lauric acid	about 25% 1,3-propanediol + about 10% benzoic acid

The pH of the concentrates of the antimicrobial mixtures of the present invention preferably have a pH below about 9.

[0037] In one embodiment, the antimicrobial mixtures of the present invention are used at a concentration of from about 0.1% to about 2% by weight.

[0038] In one preferred embodiment, the antimicrobial mixture includes caprylic acid and a waxy fatty acid (for instance, lauric acid). The inventors have found that caprylic acid facilitates solubilization and stability of the waxy fatty acid thereby enhancing its antimicrobial efficacy.

[0039] The antimicrobial mixtures and compositions of the present invention may be free or substantially free of oils.

[0040] Another embodiment is a method of killing and/or inhibiting the growth of microorganisms on a substrate or in or on a product by applying an effective amount of the antimicrobial composition of the present invention to the substrate or the product.

[0041] Yet another embodiment is a product comprising an antimicrobial, preservative, bactericidal, and/or fungicidal effective amount of the antimicrobial composition of the present invention. The product may be a solid or liquid. The antimicrobial compositions of the present invention are particularly effective as preservatives for personal care products.

[0042] Yet another embodiment is a method of preserving a product (e.g., a personal care product) by incorporating a preservative effective amount of the antimicrobial composition of the present invention into the product.

[0043] Yet another embodiment is a product (such as a shampoo) comprising a preservative effective amount of the antimicrobial composition of the present invention. The product is generally substantially free or completely free of parabens (such as methylparaben, ethylparaben, and propylparaben). The product may be, for example, a household (e.g., personal care), industrial, or institutional product. Preferred personal care products include, but are not limited to, shampoos, lotions (e.g., body lotions), conditioners, and soaps. Suitable household products include, but are not limited to, fabric softeners, laundry detergents, and hard surface cleaners. According to one embodiment, the product contains less than about 2, 1.5, 1, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, or 0.01% by weight of parabens, based upon 100% total weight of product. According to one embodiment, the product does not contain a preservative effective amount of a preservative other than components (a) and (b) above. According to another embodiment, the only preservatives in the product are components (a) and (b). According to yet another embodiment, the product is all natural. According to yet another embodiment, the product contains less than a smelling or coloring effective amount of the antimicrobial composition.

[0044] In one embodiment, the product (for example, a shampoo) has a pH below about 8.

[0045] The components of these antimicrobial mixtures are natural thickening agents. Accordingly, they can be incorpo-

rated into formulations in a thickening effective amount (for example, to thicken a shampoo or other personal care product).

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0046] The term "microorganisms" includes, but is not limited to, bacteria, fungi, yeasts, algae, insects, and pests.

[0047] The term "personal care products" refers to products intended for application to the human body, such as to skin, hair, and nails, including, but not limited to, shampoos, conditioners, creams, lotions (such as body lotions), cosmetics, and soaps.

[0048] Components for the Antimicrobial Mixture

[0049] The natural or naturally derived fatty acid may be a waxy fatty acid. Suitable natural or naturally derived fatty acids include, but are not limited to, lauric acid, caprylic acid, capric acid, palmitic acid, and any combination of any of the foregoing. In one preferred embodiment, the antimicrobial mixture contains caprylic acid and a waxy fatty acid (such as lauric acid).

[0050] Suitable natural or naturally derived products include, but are not limited to, 1,3-propanediol (natural or naturally-derived), glycereth-2 cocoate, benzyl alcohol (naturally derived), glycerin, and any combination of any of the foregoing. A preferred natural or naturally derived product is 1,3-propanediol (natural or naturally-derived).

[0051] Suitable alcoholic solvents include, but are not limited to, ethylhexyl glycerin, phenoxyethanol, caprylyl glycols, pentylene glycol, hexylene glycol, and any combination of any of the foregoing.

[0052] Suitable organic acids and their salts include, but are not limited to, sorbic acid or a salt thereof (for example, potassium sorbate), benzoic acid or a salt thereof (for example, sodium benzoate), citric acid or a salt thereof, and any combination of any of the foregoing. Suitable salts of organic acids (such as sorbic acid and benzoic acid) include, but are not limited to, alkali metal or alkali earth metal salts, such as potassium and sodium.

Examples of Preferred Mixtures

[0053] Preferred mixtures include, but are not limited to, those in the table below. Preferred concentrations and preferred weight ratios are also provided in the table.

Mixture No.	Component (a)	Component (b)	Preferred Weight Ratio of component (a) to (b)
1	From about 30% to about 60% caprylic acid and from about 5% to about 35% lauric acid	From about 10% to about 40% 1,3-propanediol and from about 5% to about 10% potassium sorbate	about 0.02:2 to about 0.025:2
2	From about 30% to about 65% caprylic acid and from about 20% to about 40% lauric acid	From about 10% to about 40% 1,3-propanediol	about 0.02:2 to about 0.025:2
3	From about 45% to about 75% caprylic acid	From about 15% to about 45% glycereth-2 cocoate and from about 5% to about 25% ethylhexyl glycerin	about 0.02:2 to about 0.025:2
4	From about 35% to about 55% caprylic acid and from about 5% to about 35% lauric acid	From about 10% to about 40% glycereth-2 cocoate and from about 5% to about 35% lactic acid	about 0.02:2 to about 0.025:2
5	From about 55% to about 85% caprylic acid	From about 15% to about 45% lactic acid	about 0.02:2 to about 0.025:2
6	From about 65% to about 95% 1,3-propanediol	From about 5% to about 25% ethylhexyl glycerin and from about 5% to about 35% potassium sorbate	about 0.02:2 to about 0.025:2

Antimicrobial Compositions

[0054] The antimicrobial compositions of the present invention are useful as antimicrobial, fungicidal, and bactericidal agents (such as against allergens, tree and plant fungi, and plant and tree bacteria) and as preservatives in the papermaking, textile, agricultural, and coating industries and in personal care, household, industrial, and institutional products. The antimicrobial composition may be incorporated into substrates susceptible to microbial growth to preserve them. For example, the preservative system may be incorporated into or be a personal care product, such as a shampoo, conditioner, cream, lotion (such as body lotion), cosmetic, or soap; a household product, such as a fabric softener, laundry detergent, or hard surface cleaner; or an industrial product, such as paint, coatings, wood, textile, adhesive, sealant, leather, rope, paper, pulp, paper board, sheet rock, ceiling tiles, plastic, fuel, petroleum, oil, rubber working fluid, metal working fluid, starches (such as pet food starch), or mineral slurry, such as a slurry of clay, calcium carbonate, or titanium oxide (TiO_2).

[0055] Generally, the product contains an antimicrobial, preservative, bactericidal, and/or fungicidal effective amount of the antimicrobial composition. According to one embodiment, the product contains from about 0.01 to about 2.0% by weight of each component of the antimicrobial composition, based upon 100% total weight of product. According to another embodiment, the product includes from about 0.1 to about 1 or 2% by weight of the antimicrobial composition, based upon 100% weight of total product.

Preservative Systems

[0056] The mixture of components discussed above (hereinafter referred to as "the preservative system") are useful as antimicrobial, fungicidal, and bactericidal agents (such as against allergens, tree fungi, and tree bacteria) and as preservatives in the papermaking, textile, agricultural, and coating industries and in personal care, household, industrial, and institutional products. The preservative system may be incorporated into substrates susceptible to microbial growth to preserve them. For example, the preservative system may be incorporated into or be a personal care product, such as a shampoo, conditioner, cream, lotion (such as body lotion), cosmetic, or soap; a household product, such as a fabric softener, laundry detergent, or hard surface cleaner; or an

industrial product, such as paint, coatings, wood, textile, adhesive, sealant, leather, rope, paper, pulp, paper board, sheet rock, ceiling tiles, plastic, fuel, petroleum, oil, rubber working fluid, metal working fluid, starches (such as pet food starch), or mineral slurry, such as a slurry of clay, calcium carbonate, or titanium oxide (TiO_2).

[0057] Generally, the antimicrobial composition and preservative system of the present invention acts quickly (e.g., reduces the microorganism (e.g., bacteria and/or fungi) count by 95, 99, 99.9, or 99.99% typically within an hour) and maintains efficacy (e.g., maintains less than 10 cfu/g) over long periods of time (e.g., for at least 7, 10, 14, or 28 days). The term "preservative effective amount" refers to an amount of the preservative system which maintains the microorganism count below 1000, 100, or 10 cfu/g for at least 1, 4, 7, 10, 14, or 28 days.

[0058] The antimicrobial composition and preservative system may include a solvent, such as water and water miscible solvents, including, but not limited to, alcohols (e.g., methanol, ethanol, propanol, iso-propanol, and butanol), glycols (e.g, glycerin, diglycerin, butylene glycol, butoxydiglycol, propylene glycol, and dipropylene glycol), esters, ethers, polyethers, and any combination of any of the foregoing. For example, the solvent may comprise water and one or more glycol and/or one or more alcohol, such as glycerin, phenoxyethanol, benzyl alcohol, or ethanol. A specific solvent system comprises water and a glycol, such as glycerin. A second specific solvent system comprises water and an alcohol, such as ethanol.

[0059] Other adjuvants may be included in the antimicrobial composition and preservative system as known to one of ordinary skill in the art. Suitable adjuvants include, but are not limited to, preservatives; solubilizing agents; chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and salts thereof and zeolites; surfactants, such as cationic, anionic, nonionic, and amphoteric surfactants; antioxidants, such as butylated hydroxyanisole (BHA) and butylhydroxytoluene (BHT); amine oxides; tertiary amines; zinc compounds; hydrotropes; fluoride compounds; magnesium salts; calcium salts; carboxylic acids; phosphates; phosphonates; formaldehyde donors; glycereth-7; myristyl myristate; glutaraldehydes; biguanides; natural products, such as geraneol, usnic acid, and tea tree oils; and any combination of any of the foregoing. Suitable preservatives include, but are not limited to, quaternary ammonium chlorides; quaternary ammonium carbonates; benzalkonium chloride; iodine containing compounds, such as 3-iodo-2-propynyl butyl carbamate (IPBC); hydantoins, such as dimethylhydantoin and halogenated hydantoins; isothiazolinones; parabens, such as methylparaben, ethylparaben, and propylparaben; dehydroacetic acid and salts thereof; isocil; chloroxylenol; chlorhexidine; phenoxyethanol; benzyl alcohol; phenethyl alcohol; benzoic acid and salts thereof such as sodium benzoate; chlorobutanol; sorbic acid and salts thereof; triclosan; triclocarban; and any combination of any of the foregoing.

[0060] The antimicrobial composition and preservative system may be incorporated into an aqueous or oil based system or an emulsion. A suitable solvent for an oil based system is phenoxyethanol and/or benzyl alcohol.

[0061] In one embodiment, the antimicrobial composition is comprised of all natural products.

[0062] The antimicrobial composition can be a liquid or a solid.

[0063] When the synergistic mixture contains only two components (i.e., two of (a), (b), and (c)) from the list above, the weight ratio of the first component to the second component typically ranges from about 0.01:100 to about 100:0.01, preferably ranges from about 0.1:20 to about 20:0.1, and more preferably ranges from about 1:10 to about 10:1. When the synergistic mixture contains three components, the third component can be in any amount, but typically the weight ratio of the third component to either of the first two components is from about 0.01:100 to about 100:0.01.

[0064] To prepare a formulation containing the product of the present invention, a concentrate of the antimicrobial composition and preservative system is generally first prepared. The concentrate may include from about 0.01 to about 100% by weight of the antimicrobial composition and preferably contains from about 5 to about 80% by weight of the antimicrobial composition, based upon 100% total weight of concentrate. For a two-component antimicrobial composition, the concentrate broadly contains from about 0.01 to about 99.99% by weight of the first component (e.g., component (a)) and from about 99.99% to about 0.01% by weight of the second component (i.e., component (b)) (based upon 100% total weight of concentrate). Table A illustrates the components and the ranges of components present in a typical concentrate for the two-component antimicrobial mixtures (based upon 100% total weight of concentrate).

TABLE A

Ranges	Component (a)	Component (b)
Broad	from about 0.01% to about 99.99%	from about 99.9% to about 0.01%
Preferred	from about 5 to about 95%	from about 95% to about 5%

[0065] Table B illustrates the components and the ranges of components present in a typical concentrate for the three-component antimicrobial mixtures (based upon 100% total weight of concentrate).

TABLE B

Ranges	Component (a) [1,3-propanediol]	Component (b) [alcoholic solvent]	Component (c) [organic acid or salt thereof]
Broad	From about 0.01% to about 70%	From about 0.01% to about 70%	From about 0.01% to about 70%
Preferred	From about 5% to about 50%	From about 5% to about 50%	From about 5% to about 50%

[0066] Before use, the concentrate is diluted, preferably with the same solvent as was used in the concentrate, and/or incorporated into a product. Use dilutions of the composition typically comprise an antimicrobial, preservative, fungicidally, or bactericidally effective amount of the antimicrobial composition.

[0067] Generally, use dilutions contain from about 0.0001% or 0.01% to about 2% by weight of the concentrate. According to one preferred embodiment, use dilutions contain from about 0.1 to about 1% by weight of the concentrate. In more preferred embodiments, the use dilution contains 0.2, 0.25 or 0.30% by weight of the concentrate. The use dilution generally contains from about 0.01, to about 2.0% by weight of each antimicrobial ingredient, based upon 100% total weight of use dilution. According to a preferred embodiment,

the antimicrobial composition contains from about 0.001 to about 10%, preferably from about 0.01 to about 1%, and more preferably from about 0.05 to about 0.5% by weight of each antimicrobial ingredient (e.g., caprylic acid and/or lauric acid). Table C illustrates the components and generally the ranges of components present in the use dilution (based upon 100% total weight of use dilution) made from a two-component antimicrobial mixture.

TABLE C

Ranges	Component (a)	Component (b)
Broad	From about 0.001% to about 10%	From about 0.001% to about 10%
Preferred	From about 0.01% to about 5%	From about 0.01% to about 5%
More Preferred	From about 0.05% to about 2%	From about 0.05% to about 2%

[0068] Table D illustrates the components and generally the ranges of components present in the use dilution (based upon 100% total weight of use dilution) made from a three-component antimicrobial mixture.

TABLE D

Ranges	Component (a) (1,3-propanediol)	Component (b) (alcoholic solvent)	Component (c) (caprylic acid or salt thereof)
Broad	from about 0.001% to about 10%	from about 0.001% to about 10%	from about 0.001% to about 10%
Preferred	from about 0.01% to about 5%	from about 0.01% to about 5%	from about 0.01% to about 5%
More Preferred	from about 0.05% to about 2%	from about 0.05% to about 2%	from about 0.05% to about 2%

[0069] In another embodiment, the use dilution includes from about 0.01 to about 1% by weight of component (a), and from about 0.01 to about 1% by weight of component (b). In yet another embodiment, the use dilution includes from about 0.05 to about 0.5% by weight of component (a), and from about 0.05 to about 0.5% by weight of component (b).

[0070] According to another embodiment, the aforementioned antimicrobial composition is incorporated into a product at a concentration of about 0.1 to about 1 or 2% by weight, based upon 100% total weight of product.

[0071] Another embodiment of the present invention is a method for inhibiting the growth of microorganisms, bacteria (e.g., *S. aureus* (ATCC #6538), *P. aeruginosa* (ATCC #9027), and *E. coli* (ATCC #8739)), and/or fungi (including plant and tree fungi) (e.g., *Candida albicans*, *Aspergillus niger* and *Phytophthora ramrum*) on a substrate by applying an antimicrobial, preservative, bactericidal, or fungicidal effective amount of the antimicrobial composition of the present invention to the substrate. The antimicrobial composition may be applied to the substrate by any method known in the art including, but not limited to, brushing, dipping, soaking, vacuum impregnation, and pressure treatment.

[0072] The antimicrobial composition of the present invention may be prepared by mixing the antimicrobial components, and optionally, solvents, and adjuvants. The mixture may be heated and/or stirred to expedite mixing.

EXAMPLES

Example 1

[0073] The solubility and stability of 20% and 25% lauric acid in glycereth 2-cocoate, 1,3-propanediol, caprylic acid, and certain mixtures of them was determined. The results are shown below.

Solvent	Solubility of 20% Lauric Acid	Solubility of 25% Lauric Acid
Glycereth 2- Cocoate	Not Soluble	Not Soluble
1,3 Propanediol	Not Soluble	Not Soluble
Caprylic acid	Soluble Stable	Soluble Stable
Caprylic acid – Glycereth 2- Cocoate	Soluble Stable	Soluble Stable
Caprylic acid + 1,3 Propanediol	Soluble Stable	Soluble Stable

Example 2

[0074] The following compounds and mixtures were added to a DEA/sulfate shampoo system to assess their ability to act as thickeners. The results are provided below.

Compound or Mixture	Thicken DEA Sulfate Shampoo Systems without salt
5% Glycereth 2- Cocoate	No
5% 1,3 Propanediol	No
5% Lauric Caprylic acid	Yes
2% Lauric Caprylic acid + Glycereth 2- Cocoate	Yes
2% Lauric Caprylic acid + 1,3 Propanediol	Yes

[0075] All references, patent applications, and patents cited herein are hereby incorporated by reference.

1. An antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

(a) (i) two or more fatty acids, each of which is natural or naturally derived, and

(ii) a fatty acid and anisic acid, each of which is natural or naturally derived; and

(b) at least one of

(i) a natural or naturally derived product,

(ii) an alcoholic solvent, or

(iii) an organic acid or a salt thereof.

2. The antimicrobial composition of claim **1**, wherein the composition is substantially free of parabens, formaldehyde donors, and isothiazolinones.

3. The antimicrobial composition of claim **1**, wherein the composition is free of parabens.

4. The antimicrobial composition of claim **1**, wherein the natural or naturally derived fatty acids are selected from lauric acid, caprylic acid, capric acid, palmitic acid, and any combination of any of the foregoing.

5. The antimicrobial composition of claim **1**, wherein the natural or naturally derived product is selected from 1,3-propanediol (natural or naturally-derived), glycereth-2 cocoate, benzyl alcohol (naturally derived), glycerin, and any combination of any of the foregoing.

6. The antimicrobial composition of claim **1**, wherein the natural or naturally derived product is 1,3-propanediol (natural or naturally-derived).

7. The antimicrobial composition of claim **1**, wherein the alcoholic solvent is selected from ethylhexyl glycerin, phenoxyethanol, caprylyl glycols, pentylene glycol, hexylene glycol, and any combination of any of the foregoing.

8. The antimicrobial composition of claim **1**, wherein the organic acid is selected from sorbic acid, benzoic acid, citric acid, and any combination of any of the foregoing.

9. The antimicrobial composition of claim **1**, wherein the mixture comprises (a) lauric acid and caprylic acid, and (b) glycereth-2 cocoate or 1,3-propanediol.

10. An antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

(a) caprylic acid,

(b) at least one waxy fatty acid, each of which is natural or naturally derived, and

(c) at least one of

(i) a natural or naturally derived product,

(ii) an alcoholic solvent, or

(iii) an organic acid.

11. The antimicrobial composition of claim **10**, wherein the caprylic acid is natural or naturally derived.

12. An antimicrobial composition consisting essentially of an antimicrobial effective amount of a mixture consisting essentially of two or more fatty acids, each of which is natural or naturally derived.

13. The antimicrobial composition of claim **12**, wherein the natural or naturally derived fatty acids are selected from lauric acid, caprylic acid, capric acid, palmitic acid, and any combination of any of the foregoing.

14. The antimicrobial composition of claim **12**, wherein the mixture consists essentially of caprylic acid and lauric acid.

15. The antimicrobial composition of claim **12**, wherein the mixture consists essentially of at least about 50% by weight of caprylic acid.

16. An antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

(a) caprylic acid, which is natural or naturally derived,

(b) a natural or naturally derived product,

(c) an alcoholic solvent, and

(d) optionally, an organic acid or a salt thereof.

17. The antimicrobial composition of claim **16**, wherein the mixture comprises caprylic acid, glycereth 2-cocoate, and ethylhexyl glycerin.

18. An antimicrobial composition comprising an antimicrobial effective amount of a mixture comprising:

(a) 1,3-propanediol (natural or naturally-derived),

(b) an alcoholic solvent, and

(c) optionally, an organic acid or a salt thereof.

19. The antimicrobial composition of claim **18**, wherein the mixture comprises (a) 1,3-propanediol, which is natural or naturally-derived, (b) ethylhexyl glycerin, and (c) potassium sorbate or benzoic acid.

20. The antimicrobial composition of claim **18**, wherein the mixture comprises 1,3-propanediol (natural or naturally-derived), natural benzyl alcohol, and optionally, caprylhydroxamic acid.

21. The antimicrobial composition of claim **1**, wherein the mixture is present at a concentration of from about 0.01 to about 2% by weight, based on 100% total weight of the composition.

22. A method of killing and/or inhibiting the growth of microorganisms on a substrate comprising applying an effective amount of the antimicrobial composition of claim **1**.

23. The method of claim **20**, wherein the microorganisms are selected from *S. aureus*, *P. aeruginosa*, *E. coli*, *Candida albicans*, *Aspergillus niger* and *Phytophthora ramrum*.

24. The method of claim **22**, wherein the substrate is a product other than a foodstuff, pharmaceutical, or cosmetic.

25. A product other than a foodstuff, pharmaceutical, or cosmetic comprising a preservative effective amount of the antimicrobial composition of claim **1**, wherein the product is substantially free of parabens.

26. The product of claim **25**, wherein the product is a household, industrial, or institutional product.

27. The product of claim **25**, wherein the product is a personal care product.

28. The product of claim **27**, wherein the personal care product is a shampoo, body lotion, conditioner, or soap.

29. The product of claim **25**, wherein the product comprises less than a smelling or coloring effective amount of the antimicrobial composition.

* * * * *

Electronic Patent Application Fee Transmittal

Application Number:	16262898
Filing Date:	30-Jan-2019
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	Victor Jay Castellucci/Valerie Dotson
Attorney Docket Number:	INLX.0198U1/484809

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	1806	1	260	260
RCE- 2ND AND SUBSEQUENT REQUEST	1820	1	2000	2000
		Total in USD ($)		**2260**

Electronic Acknowledgement Receipt

EFS ID:	40992334
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	171052
Filer:	Victor Jay Castellucci/Valerie Dotson
Filer Authorized By:	Victor Jay Castellucci
Attorney Docket Number:	INLX.0198U1/484809
Receipt Date:	30-OCT-2020
Filing Date:	30-JAN-2019
Time Stamp:	12:30:02
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$2260
RAM confirmation Number	E20200TC31085690
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	INLX_0198U1_484809_RCE_and_IDS_Transmittal.pdf	115245 a18147f5de81c1ea4f94f42c464bb8e766e5deb0	no	2
Warnings:					
Information:					
2	Request for Continued Examination (RCE)	INLX_0198U1_484809_RCE.pdf	1353169 698a4f07f8ead50f3d1a6799a8e806a2dc64f050	no	3
Warnings:					
Information:					
3	Information Disclosure Statement (IDS) Form (SB08)	INLX_0198U1_484809_Information_Disclosure_Statement.pdf	1041938 ca94385089bea1b7cdc359b43effcbb7923eb194	no	4
Warnings:					
Information:					
4	Non Patent Literature	INLX_0198U1_484809_Non_Final_Office_Action_INLX0198U2.pdf	315829 432073dc294614171d3df00e8b0bdd004f62ebaa	no	10
Warnings:					
Information:					
5	Non Patent Literature	INLX_0198U1_484809_Third_Party_Submission_16682059.pdf	78329 28c8953fe6b47ac6df4b62965e8ba0c761e7d105	no	3
Warnings:					
Information:					
6	Non Patent Literature	INLX_0198U1_484809_Balls_E-Mail_2020-10-27.pdf	1443895 d83becde5a8556860d2f48315d1d643281da5c79	no	2
Warnings:					
Information:					

7	Other Reference-Patent/App/Search documents	INLX_0198U1_484809_Peters.pdf	1637691 dfdb68491044 3bfbbc66db0e2a06ac5943d1babf	no	36
Warnings:					
Information:					
8	Other Reference-Patent/App/Search documents	INLX_0198U1_484809_Lutz.pdf	272301 152ba2a28e0b64fd1e7a742341d3259cc101ace7	no	7
Warnings:					
Information:					
9	Fee Worksheet (SB06)	fee-info.pdf	32415 c5ad4587f69cc60557b97bd37c7f5945a925facb	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	6290812	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor: Rocco V. Burgo

Application No.: 16/262,898 Art Unit: 1662

Filing Date: January 30, 2019 Examiner: Yate K. CUTLIFF

Confirmation No.: 3410 Docket No: INLX.0198U1/484809

Title: **Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same**

EFS Web
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

REQUEST FOR CONTINUED EXAMINATION
INFORMATION DISCLOSURE STATEMENT UNDER §1.97(b)

Pursuant to 37 CFR § 1.56 and in accordance with 37 CFR §§ 1.97-1.98, information relating to the above-identified application is hereby disclosed. Inclusion of information in this statement is not to be construed as an admission that this information is material as that term is defined in 37 CFR § 1.56(b).

Applicants have filed this Request for Continued Examination Under 37 C.F.R. § 1.114 and accompanying Information Disclosure Statement after receiving a telephone call from Practitioner R. James Balls of the law firm Polsinelli PC. Mr. Balls purportedly telephoned the undersigned on behalf of an unnamed client who has been "interested in" the prosecution of this matter. Mr. Balls followed up his telephone inquiry with the email communication (submitted herewith as NPL3), in which it is alleged that the prosecution file wrappers of U.S. Appl. No. 16/262,902 and U.S. Appl. No. 16/682,059 are relevant to the patentability of the previously allowed, and now pending claims of the present application.

The Non-Final Office Action with a mailing date of September 17, 2020 issued in U.S. Appl No. 16/262,902 (Examiner - NANNETTE HOLLOMAN) is submitted herewith as NPL1. Applicants note that the prior art cited in NPL1 has already been made of record in this matter,

except for the Lutz reference (US 20120282207 A1), which is submitted herewith as U.S. Patent Application Pub. Ref. No. 1.

The third-party Submission Under 37 CFR 1.290 filed in U.S. Patent Application No. 16/682,059 on September 8, 2020 by Practitioner Daniel Altman is submitted herewith as NPL2. Applicants note that the prior art cited in NPL2 has already been made of record in this matter, except for the Peters reference (US 8450543), which is submitted herewith as U.S. Patent Ref. No. 1.

Please charge any deficiency or credit any overpayment to Deposit Account No. 50-3632.

2020-10-30
Date

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Doc Code: PET.AUTO Document Description: Petition automatically granted by EFS-Web	PTO/SB/140 U.S. Patent and Trademark Office Department of Commerce

Electronic Petition Request	**PETITION TO WITHDRAW AN APPLICATION FROM ISSUE AFTER PAYMENT OF THE ISSUE FEE UNDER 37 CFR 1.313(c)**
Application Number	16262898
Filing Date	30-Jan-2019
First Named Inventor	Rocco Burgo
Art Unit	1622
Examiner Name	YATE CUTLIFF
Attorney Docket Number	INLX.0198U1/484809
Title	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

An application may be withdrawn from issue for further action upon petition by the applicant. To request that the Office withdraw an application from issue, applicant must file a petition under this section including the fee set forth in § 1.17(h) and a showing of good and sufficient reasons why withdrawal of the application from issue is necessary.

APPLICANT HEREBY PETITIONS TO WITHDRAW THIS APPLICATION FROM ISSUE UNDER 37 CFR 1.313(c).

A grantable petition requires the following items:
(1) Petition fee; and
(2) One of the following reasons:
(a) Unpatentability of one or more claims, which must be accompanied by an unequivocal statement that one or more claims are unpatentable, an amendment to such claim or claims, and an explanation as to how the amendment causes such claim or claims to be patentable;
(b) Consideration of a request for continued examination in compliance with § 1.114 (for a utility or plant application only); or
(c) Express abandonment of the application. Such express abandonment may be in favor of a continuing application, but not a CPA under 37 CFR 1.53(d).

Petition Fee

- ○ Small Entity
- ○ Micro Entity
- ◉ Regular Undiscounted

Reason for withdrawal from issue

◯ One or more claims are unpatentable ◉ Consideration of a request for continued examination (RCE) (List of Required Documents and Fees) ◯ Applicant hereby expressly abandons the instant application (any attorney/agent signing for this reason must have power of attorney pursuant to 37 CFR 1.32(b)).
RCE request,submission, and fee. ☒ I certify, in accordance with 37 CFR 1.4(d)(4) that : The RCE request ,submission, and fee have already been filed in the above-identified application on 2020.10.30 ☐ Are attached.
THIS PORTION MUST BE COMPLETED BY THE SIGNATORY OR SIGNATORIES I certify, in accordance with 37 CFR 1.4(d)(4) that I am: ◉ An attorney or agent registered to practice before the Patent and Trademark Office who has been given power of attorney in this application. ◯ An attorney or agent registered to practice before the Patent and Trademark Office, acting in a representative capacity. ◯ A sole inventor ◯ A joint inventor; I certify that I am authorized to sign this submission on behalf of all of the inventors as evidenced by the power of attorney in the application ◯ A joint inventor; all of whom are signing this e-petition

Signature	/Victor Castellucci/
Name	Victor Castellucci
Registration Number	43535

Electronic Patent Application Fee Transmittal

Application Number:	16262898
Filing Date:	30-Jan-2019
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Filer:	Victor Jay Castellucci/Valerie Dotson
Attorney Docket Number:	INLX.0198U1/484809

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
PETITION FEE- 37 CFR 1.17(H) (GROUP III)	1464	1	140	140
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension-of-Time:				
Miscellaneous:				
			Total in USD ($)	**140**

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

Decision Date : October 30, 2020

In re Application of :

Rocco Burgo

DECISION ON PETITION

UNDER CFR 1.313(c)(2)

Application No : 16262898

Filed : 30-Jan-2019

Attorney Docket No : INLX.0198U1/484809

This is an electronic decision on the petition under 37 CFR 1.313(c)(2), filed October 30, 2020 , to withdraw the above-identified application from issue after payment of the issue fee.

The petition is **GRANTED.**

The above-identified application is withdrawn from issue for consideration of a submission under 37 CFR 1.114 (request for continued examination). See 37 CFR 1.313(c)(2).

Petitioner is advised that the issue fee paid in this application cannot be refunded. If, however, this application is again allowed, petitioner may request that it be applied towards the issue fee required by the new Notice of Allowance.

Telephone inquiries concerning this decision should be directed to the Patent Electronic Business Center (EBC) at 866-217-9197.

This application file is being referred to Technology Center AU 1622 for processing of the request for continuing examination under 37 CFR 1.114 .

Office of Petitions

Electronic Acknowledgement Receipt

EFS ID:	40995655
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	171052
Filer:	Victor Jay Castellucci/Valerie Dotson
Filer Authorized By:	Victor Jay Castellucci
Attorney Docket Number:	INLX.0198U1/484809
Receipt Date:	30-OCT-2020
Filing Date:	30-JAN-2019
Time Stamp:	13:42:37
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$140
RAM confirmation Number	E20200TD42336988
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Petition automatically granted by EFS	petition-request.pdf	31783 35d25dca336f7434dbf5c848e39d9411b2324fb7	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30978 161dfc06ffa7e7977762281caf378cd01ef43948	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	62761		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

171052 7590 11/25/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

EXAMINER
CUTLIFF, YATE KAI RENE

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 11/25/2020

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$1000.00	$200	02/25/2021

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

171052 7590 11/25/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$1000.00	$200	02/25/2021

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑ Issue Fee ❑ Publication Fee (if required) ❑ Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

171052 7590 11/25/2020

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036

EXAMINER	
CUTLIFF, YATE KAI RENE	
ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 11/25/2020

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/262,898	Applicant(s) Burgo et al.	
	Examiner YATE K CUTLIFF	Art Unit 1622	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to RCE of 10/30/2020.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1-34 and 88-91 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date 10/30/2020.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

DETAILED ACTION

Notice of Pre-AIA or AIA Status

1. The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Continued Examination Under 37 CFR 1.114

2. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after allowance or after an Office action under *Ex Parte Quayle*, 25 USPQ 74, 453 O.G. 213 (Comm'r Pat. 1935). Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, prosecution in this application has been reopened pursuant to 37 CFR 1.114. Applicant's submission filed on October 30, 2020 has been entered.

Information Disclosure Statement

3. The information disclosure statement (IDS) submitted on October 30, 2020 was filed after the mailing date of the Notice of Allowance on September 23, 2020. The submission is in compliance with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

Allowable Subject Matter

4. Claims 1 – 34 and 88 – 91 are allowed.

5. The following is an examiner's statement of reasons for allowance: Claims are allowed for the reasons set out in the Notice of Allowance mailed April 13, 2020.

6. The Examiner considered the cited references and conducted a thorough search of the appropriate data bases for the claimed subject matter and did not discover any

reference which anticipates the claimed subject matter or would form the basis for concluding that the claimed subject matter would have been obvious.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusion

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to YATE K. CUTLIFF whose telephone number is (571)272-9067. The examiner can normally be reached on Monday-Friday (8:30 - 5:30).

Examiner interviews are available via telephone, in-person, and video conferencing using a USPTO supplied web-based collaboration tool. To schedule an interview, applicant is encouraged to use the USPTO Automated Interview Request (AIR) at http://www.uspto.gov/interviewpractice.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon Fetterolf can be reached on (571) 272 - 2919. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only.

For more information about the PAIR system, see https://ppair-my.uspto.gov/pair/PrivatePair. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/YATE' K CUTLIFF/
Primary Examiner, Art Unit 1622

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC						
Symbol					Type	Version
C07C	/	29	/	04	F	2013-01-01
C07C	/	31	/	20	I	2013-01-01
C07C	/	29	/	80	I	2013-01-01
B01J	/	23	/	06	I	2013-01-01
B01J	/	37	/	08	I	2013-01-01
B01J	/	21	/	04	I	2013-01-01
C11D	/	3	/	2044	I	2013-01-01
C07C	/	1	/	24	I	2013-01-01
C07C	/	29	/	48	I	2013-01-01
C07C	/	11	/	02	I	2013-01-01
C07C	/	11	/	107	I	2013-01-01
B01J	/	2523	/	27	A	2013-01-01
C07B	/	41	/	02	A	2013-01-01
C07B	/	63	/	00	A	2013-01-01
B01J	/	2523	/	31	A	2013-01-01
A61L	/	2	/	18	A	2013-01-01
A01N	/	31	/	02	A	2013-01-01
A61K	/	8	/	345	A	2013-01-01
A61Q	/	5	/	00	A	2013-01-01
A61Q	/	11	/	00	A	2013-01-01
A61Q	/	19	/	00	A	2013-01-01
C11D	/	3	/	48	A	2013-01-01
C07C	/	2521	/	04	A	2013-01-01

CPC Combination Sets								
Symbol					Type	Set	Ranking	Version
C07C	/	1	/	24	I	1	1	2013-01-01
C07C	/	11	/	02	I	1	2	2013-01-01
C07C	/	29	/	48	I	2	1	2013-01-01
C07C	/	31	/	20	I	2	2	2013-01-01

NONE (Assistant Examiner) (Date)		Total Claims Allowed: 38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622 (Primary Examiner) (Date)	19 November 2020	O.G. Print Claim(s) 1	O.G. Print Figure 1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CPC Combination Sets									
Symbol					**Type**	**Set**	**Ranking**	**Version**
C07C	/	29	/	80	I	3	1	2013-01-01
C07C	/	31	/	20	I	3	2	2013-01-01

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	19 November 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

INTERNATIONAL CLASSIFICATION					
CLAIMED					
C07C	/	29	/	04	
C07C	/	29	/	48	

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	38	
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	19 November 2020	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	1

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
1	1	13	13	25	25		37		49		61		73		85
2	2	14	14	26	26		38		50		62		74		86
3	3	15	15	27	27		39		51		63		75		87
4	4	16	16	28	28		40		52		64		76	35	88
5	5	17	17	29	29		41		53		65		77	36	89
6	6	18	18	30	30		42		54		66		78	37	90
7	7	19	19	31	31		43		55		67		79	38	91
8	8	20	20	32	32		44		56		68		80		
9	9	21	21	33	33		45		57		69		81		
10	10	22	22	34	34		46		58		70		82		
11	11	23	23		35		47		59		71		83		
12	12	24	24		36		48		60		72		84		

NONE		**Total Claims Allowed:**
(Assistant Examiner)	(Date)	38
/YATE' K CUTLIFF/ Primary Examiner, Art Unit 1622	19 November 2020	O.G. Print Claim(s) / O.G. Print Figure
(Primary Examiner)	(Date)	1 / 1

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020	05/18/2020	09/08/2020	11/19/2020				
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6	6	✓	=	=	=	=				
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Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	**Art Unit**
	YATE K CUTLIFF	1622

CLAIM		DATE								
Final	Original	08/01/2019	04/03/2020	05/18/2020	09/08/2020	11/19/2020				
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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

CPC - Searched*		
Symbol	Date	Examiner
C07C 29/04, 48	09/08/2020	ykc
C07C 31/20	09/08/2020	ykc
C07C 33/025	09/08/2020	ykc
C07C 2521/04	04/03/2020	ykc
B01J 21/04	09/08/2020	ykc
B01J 23/06	09/08/2020	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	04/03/2020	ykc
C07B 41/02	04/03/2020	ykc

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/262,898	Burgo et al.
	Examiner	Art Unit
	YATE K CUTLIFF	1622

Search Notes		
Search Notes	**Date**	**Examiner**
Palm Inventor Search	11/19/2020	ykc
East	11/19/2020	ykc
C07C 29/04, 48	09/08/2020	ykc
C07C 31/20	09/08/2020	ykc
C07C 33/025	09/08/2020	ykc
C07C 2521/04	05/18/2020	ykc
B01J 21/04	09/08/2020	ykc
B01J 23/06	09/08/2020	ykc
B01J 37/08	08/01/2019	ykc
C07C 11/02, 107	05/18/2020	ykc
C07B 41/02	05/18/2020	ykc

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
C07C	29/04, 48	11/19/2020	ykc
C07C	31/20	11/19/2020	ykc
C07C	33/025	11/19/2020	ykc
B01J	21/04	11/19/2020	ykc
B01J	23/06	11/19/2020	ykc

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BIB DATA SHEET

CONFIRMATION NO. 3410

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
16/262,898	01/30/2019	568	1622	INLX.0198U1/484809

APPLICANTS

Inolex Investment Corporation, Wilmington, DE

INVENTORS

Rocco V. Burgo, Mullica Hill, NJ;
Michael E. Wright, Hurricane, UT;
Gary B. Mosser, Tabernacle, NJ;
Michael J. Fevola, Belle Mead, NJ;

**** CONTINUING DATA ***************************

This appln claims benefit of 62/623,985 01/30/2018

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

02/15/2019

Foreign Priority claimed	❑ Yes ☑ No	❑ Met after Allowance	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
35 USC 119(a-d) conditions met	❑ Yes ☑ No		NJ	7	41	3
Verified and Acknowledged	/YATE KAI RENE CUTLIFF/ Examiner's Signature	Initials				

ADDRESS

Cozen O'Connor - Inolex
1200 19th St. NW
Washington, DC 20036
UNITED STATES

TITLE

Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

FILING FEE RECEIVED	FEES: Authority has been given in Paper	❑ All Fees
3980	No._____ to charge/credit DEPOSIT ACCOUNT	❑ 1.16 Fees (Filing)
	No._____ for following:	❑ 1.17 Fees (Processing Ext. of time)
		❑ 1.18 Fees (Issue)
		❑ Other _____
		❑ Credit

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S1	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:57
S2	69	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S3	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S4	69	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/07/31 10:58
S5	2	"2016007196".pn.	US-PGPUB; USPAT; USOCR; FPRS; EPO	OR	OFF	2019/07/31 11:33
S6	9,189	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:43
S7	1,392	(natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:45
S8	23	S6 and S7 and alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 12:46
S9	9,170	(method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S10	684	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and dehydration	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:50
S11	378	S10 and (natural or plant or vegetable or ferment$4 or biomass or renewable or sustainable)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 12:51

S12	125	S11 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:02
S13	125	S12 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:03
S14	9,170	((method or process or prepare or make or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S15	1,219	S14 and (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:05
S16	1,175	S15 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:05
S17	55	S14 and (terminal with (alkene or octene or pentene or hexene or heptene or nonene or decene or dodecene))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 13:07
S18	3	("20050006997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:29
S19	3	("20050069997," "7576250").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 13:30
S20	5,912	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol)))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:35
S21	2,221	S20 and (natural or plant or vegetable or ferment$4 or biomass)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:40
S22	312	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and (peracid or	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42

		formic of acetic) and (hydrogen adj peroxide)				
S23	308	S22 and @ay<="2018"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:42
S24	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/07/31 13:51
S25	3,031	C07C29/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:15
S26	5,809	C07C31/20.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S27	0	C07C33/25.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:16
S28	3,127	C07C33/025.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S29	18,997	B01J21/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:17
S30	16,230	B01J37/08.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:18

S31	4,501	B01J23/06.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:21
S32	14,742	c07c2521/04.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:22
S33	38	S25 and S28	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:23
S34	2	S20 and S33	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:24
S35	5	S28 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:25
S36	0	S25 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S37	0	S33 and S29 and S31	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/07/31 14:26
S38	1	"7385092".pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/07/31 16:49
S39	1	"20170360035".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2019/08/01 10:10

S40	13	(biodiene? or (bio adj diene?) or (bio adj alkene) or bioalkene)	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2019/08/01 10:27
S41	67	((method or prepare or synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))) and ((peracid or formic of acetic) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:13
S42	27	S41 and hydrolysis	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:13
S43	9,195	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2019/08/01 11:16
S44	886	S43 and hydrolysis	USPAT	OR	OFF	2019/08/01 11:16
S45	24	S43 and hydrolysis and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:17
S46	5	S43 and (hydroxide with hydrolysis) and ((formic adj acid) with (hydrogen adj peroxide))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2019/08/01 11:24
S47	1	"20140066666".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:26
S48	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:29
S49	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:30
S50	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S51	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/04/03 12:33
S52	2,015	c07c29/48.cpc.	US-PGPUB; USPAT; USOCR;	OR	OFF	2020/04/03 12:49

			FPRS; EPO; JPO; DERWENT; IBM_TDB			
S53	1,075	c07b41/02.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:54
S54	24,629	c07c11/02,107.cpc.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S55	32	S53 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S56	9	S55 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:55
S57	23	S52 and S53	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S58	5	S57 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:57
S59	48	S52 and S54	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/04/03 12:58
S60	6	S59 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO;	OR	OFF	2020/04/03 12:58

			JPO; DERWENT; IBM_TDB			
S77	13	("20050006997," "20060161025," "20160090331," "20170360035," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 11:20
S78	14	("20050006997," "20060161025," "20160090331," "20170360035," "7385092," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 11:31
S79	3	S78 and (alkanediol or octanediol)	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 11:49
S80	3	S78 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 11:50
S81	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/05/18 12:03
S82	14	("20050069997," "20060161025," "20160090331," "20170360035," "7385092," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 12:18
S83	15	("20050069997," "20060161025," "20070207105," "20160090331," "20170360035," "7385092," "7576250," "8345007," "9029619," "9242226," "9649626," "9732295").pn.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/05/18 12:22
S84	5	S83 and diol	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/05/18 12:23
S85	8	("2004078336," "2013077904," "2013106065," "105312044").pn.	FPRS; EPO	OR	OFF	2020/05/18 12:25
S86	5	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:28

S87	71	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S88	2	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S89	72	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/05/18 12:35
S104	7	("20030065233" | "20050065389" | "20060161025" | "20140066666" | "4234752" | "8912373" | "9856461").PN.	US-PGPUB; USPAT	OR	OFF	2020/09/08 10:08
S105	124	((swern) near (daniel)).inv.	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/09/08 10:33
S106	116	((swern) near (daniel)).inv.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 10:34
S107	1	"20080161025".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 10:38
S108	1	"20070161025".pn.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 10:39
S109	9,940	(method or process or prepare or make of synthesize or synthesis) with (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 10:40
S110	1	S104 and S109	US-PGPUB; USPAT; USOCR; FPRS	OR	OFF	2020/09/08 10:40
S111	7	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:13
S112	72	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:14
S113	3	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:14
S114	73	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/09/08 12:14
S115	25	bio near2 alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:16
S116	17	bio adj alkene	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:17
S117	5	S115 and (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:23

S118	154	1-alkene and (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:23
S119	149	S118 and @ay<="2017"	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	OFF	2020/09/08 12:24
S120	16	1-alkene same (alkanediol or hexanediol or decanediol or dodecanediol or octanediol or (vicinal adj diol))	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO	OR	OFF	2020/09/08 12:41
S143	2	("20120282207" | "8450543").PN.	US-PGPUB; USPAT	OR	OFF	2020/11/19 18:56
S144	7	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/11/19 19:30
S145	72	((("Wright") near3 ("Michael") near3 ("E"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/11/19 19:30
S146	3	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/11/19 19:31
S147	74	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	US-PGPUB; USPAT; USOCR	OR	OFF	2020/11/19 19:31

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
S61	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S62	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S63	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S64	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/04/03 13:00
S65	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S66	698	C07C31/20.cpc.	USPAT	OR	OFF	2020/04/03 13:01
S67	251	c07c29/48.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S68	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/04/03 13:04

S69	3,196	c07c11/02,107.cpc.	USPAT	OR	OFF	2020/04/03 13:04
S70	2,105	B01J21/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S71	2,140	c07c2521/04.cpc.	USPAT	OR	OFF	2020/04/03 13:05
S72	2	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S69	USPAT	OR	OFF	2020/04/03 13:07
S73	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S66	USPAT	OR	OFF	2020/04/03 13:09
S74	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S65	USPAT	OR	OFF	2020/04/03 13:10
S75	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S67	USPAT	OR	OFF	2020/04/03 13:10
S76	0	(S61 or S62 or S63 or S64) and S69 and (S70 or S71) and S68	USPAT	OR	OFF	2020/04/03 13:10
S90	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/05/18 12:40
S91	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/05/18 12:40
S92	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/05/18 12:40
S93	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/05/18 12:41
S94	3,211	c07c11/02,107.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S95	2,128	B01J21/04.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S96	2,151	c07c2521/04.cpc.	USPAT	OR	OFF	2020/05/18 12:41
S97	2	(S90 or S91 or S92) and S94 and (S95 or S96) and S94	USPAT	OR	OFF	2020/05/18 12:41
S98	418	C07C29/04.cpc.	USPAT	OR	OFF	2020/05/18 12:43
S99	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S98	USPAT	OR	OFF	2020/05/18 12:43
S100	2	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S94	USPAT	OR	OFF	2020/05/18 12:43
S101	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S98	USPAT	OR	OFF	2020/05/18 12:44
S102	97	c07b41/02.cpc.	USPAT	OR	OFF	2020/05/18 12:44
S103	0	(S90 or S91 or S92 or S93) and S94 and (S95 or S96) and S102	USPAT	OR	OFF	2020/05/18 12:44

S121	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/09/08 12:51
S122	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/09/08 12:51
S123	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/09/08 12:52
S124	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/09/08 12:52
S125	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/09/08 12:59
S126	415	C07C29/04.cpc.	USPAT	OR	OFF	2020/09/08 12:59
S127	689	C07C31/20.cpc.	USPAT	OR	OFF	2020/09/08 13:00
S128	401	C07C33/025.cpc.	USPAT	OR	OFF	2020/09/08 13:01
S129	2,166	B01J21/04.cpc.	USPAT	OR	OFF	2020/09/08 13:01
S130	514	B01J23/06.cpc.	USPAT	OR	OFF	2020/09/08 13:02
S131	0	(S121 or S122 or S123 or S124) and S126 and S129	USPAT	OR	OFF	2020/09/08 13:02
S132	0	(S121 or S122 or S123 or S124) and S126 and S130	USPAT	OR	OFF	2020/09/08 13:03
S133	0	(S121 or S122 or S123 or S124) and S127 and S129	USPAT	OR	OFF	2020/09/08 13:03
S134	0	(S121 or S122 or S123 or S124) and S127 and S130	USPAT	OR	OFF	2020/09/08 13:03
S135	0	(S121 or S122 or S123 or S124) and S128 and S129	USPAT	OR	OFF	2020/09/08 13:03
S136	0	(S121 or S122 or S123 or S124) and S128 and S130	USPAT	OR	OFF	2020/09/08 13:03
S137	261	c07c29/48.cpc.	USPAT	OR	OFF	2020/09/08 13:17
S138	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S139	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S140	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S141	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/09/08 13:18
S142	0	(S138 or S139 or S140 or S141) and S137	USPAT	OR	OFF	2020/09/08 13:18

S148	1	((("Burgo") near3 ("Rocco") near3 ("V"))).INV.	USPAT	OR	OFF	2020/11/19 19:31
S149	44	((("Wright") near3 ("Michael") near3 ("E"))).INV.	USPAT	OR	OFF	2020/11/19 19:31
S150	0	((("Mosser") near3 ("Gary") near3 ("B"))).INV.	USPAT	OR	OFF	2020/11/19 19:31
S151	28	((("Fevola") near3 ("Michael") near3 ("J"))).INV.	USPAT	OR	OFF	2020/11/19 19:32
S152	419	C07C29/04.cpc.	USPAT	OR	OFF	2020/11/19 19:34
S153	707	C07C31/20.cpc.	USPAT	OR	OFF	2020/11/19 19:35
S154	264	c07c29/48.cpc.	USPAT	OR	OFF	2020/11/19 19:35
S155	421	C07C33/025.cpc.	USPAT	OR	OFF	2020/11/19 19:35
S156	2,188	c07c2521/04.cpc.	USPAT	OR	OFF	2020/11/19 19:36
S157	2,232	B01J21/04.cpc.	USPAT	OR	OFF	2020/11/19 19:36
S158	531	B01J23/06.cpc.	USPAT	OR	OFF	2020/11/19 19:36
S159	0	(S148 0r S149 ro S150 or S151) and S152 and S157	USPAT	OR	OFF	2020/11/19 19:39
S160	0	(S148 0r S149 ro S150 or S151) and S153 and S157	USPAT	OR	OFF	2020/11/19 19:39
S161	0	(S148 0r S149 ro S150 or S151) and S154 and S157	USPAT	OR	OFF	2020/11/19 19:39
S162	0	(S148 0r S149 ro S150 or S151) and S155 and S157	USPAT	OR	OFF	2020/11/19 19:39
S163	4	(S148 0r S149 ro S150 or S151) and S156 and S157	USPAT	OR	OFF	2020/11/19 19:40
S164	0	(S148 0r S149 ro S150 or S151) and S152 and S158	USPAT	OR	OFF	2020/11/19 19:40
S165	4	(S148 0r S149 ro S150 or S151) and S153 and S158	USPAT	OR	OFF	2020/11/19 19:41
S166	0	(S148 0r S149 ro S150 or S151) and S154 and S158	USPAT	OR	OFF	2020/11/19 19:41
S167	0	(S148 0r S149 ro S150 or S151) and S155 and S158	USPAT	OR	OFF	2020/11/19 19:41
S168	3	(S148 0r S149 ro S150 or S151) and S156 and S158	USPAT	OR	OFF	2020/11/19 19:41

11/19/2020 7:44:26 PM
C:\Users\ycutliff\Documents\EAST\Workspaces\16262898.wsp

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16262898
Filing Date	2019-01-30
First Named Inventor	Rocco V. Burgo
Art Unit	1622
Examiner Name	CUTLIFF, YATE KAI RENE
Attorney Docket Number	INLX.0198U1/484809

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
/Y.K.C/	1	8450543	B2	2013-05-28	PETERS, Matthew W.	

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
/Y.K.C/	1	20120282207	A1	2012-11-08	LUTZ, Patrick J.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16262898
	Filing Date	2019-01-30
	First Named Inventor	Rocco V. Burgo
	Art Unit	1622
	Examiner Name	CUTLIFF, YATE KAI RENE
	Attorney Docket Number	INLX.0198U1/484809

/Y.K.C/	1	Non-Final Office Action with a mailing date of September 17, 2020 issued in U.S. Patent Application No. 16/262,902 (Examiner - NANNETTE HOLLOMAN)
/Y.K.C/	2	Third Party Submission Under 37 CFR 1.290 filed in U.S. Patent Application No. 16/682,059 on September 8, 2020 by DANIEL ALTMAN
/Y.K.C/	3	Email communication from Practitioner R. James Balls to Practitioner Victor Castellucci concerning the alleged relevance of the prosecution file wrappers of U.S. Appl. No. 16/262,902 and U.S. Appl. No. 16/682,059.

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EXAMINER SIGNATURE

Examiner Signature	/YATE' K CUTLIFF/	Date Considered	11/19/2020

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

OPAP AKIMA-7 DEC 0 2 2020 PATENT & TRADEMARK OFFICE

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

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171052 7590 11/25/2020

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1200 19th St. NW
Washington, DC 20036

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I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)

(Signature)

(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/30/2019	Rocco V. Burgo	INLX.0198U1/484809	3410

TITLE OF INVENTION: Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$1000.00	$200	02/25/2021

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,

(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 COZEN O'CONNOR

2

3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: INOLEX INVESTMENT CORPORATION

(B) RESIDENCE: (CITY and STATE OR COUNTRY): WILMINGTON, DELAWARE

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 50-3111

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Aaron Lukas - 59,443/ Date December 2, 2020

Typed or printed name Aaron Lukas Registration No. 59,443

PART B - FEE(S) TRANSMITTAL

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Commissioner for Patents
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INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

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Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

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(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$1000.00	$200	02/25/2021

EXAMINER	ART UNIT	CLASS-SUBCLASS
CUTLIFF, YATE KAI RENE	1622	568-860000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

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☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 COZEN O'CONNOR
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: INOLEX INVESTMENT CORPORATION

(B) RESIDENCE: (CITY and STATE OR COUNTRY): WILMINGTON, DELAWARE

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required) ☐ Advance Order - # of Copies

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

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☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 50-3111

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29

☐ Applicant asserting small entity status. See 37 CFR 1.27

☐ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Aaron Lukas - 59,443/ Date December 2, 2020

Typed or printed name Aaron Lukas Registration No. 59,443

Electronic Acknowledgement Receipt

EFS ID:	41269190
Application Number:	16262898
International Application Number:	
Confirmation Number:	3410
Title of Invention:	Natural 1,2-Alkanediols, Compositions Having Natural 1,2-Alkanediols and Processes for Making the Same
First Named Inventor/Applicant Name:	Rocco V. Burgo
Customer Number:	171052
Filer:	Aaron Scott Lukas/Valerie Dotson
Filer Authorized By:	Aaron Scott Lukas
Attorney Docket Number:	INLX.0198U1/484809
Receipt Date:	02-DEC-2020
Filing Date:	30-JAN-2019
Time Stamp:	10:26:33
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	INLX_0198U1_484809_Issue_Fee_Transmittal.pdf	1530593 cd6b0ab896bebf7dfb234722109153446ed161f8	no	1

Warnings:

Information:	
Total Files Size (in bytes):	1530593

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

United States Patent and Trademark Office

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Document Code:WFEE

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Sale Accounting Date:12/03/2020

Sale Item Reference Number	Effective Date
16262898	12/02/2020

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I2020B3006364515	1501	UTILITY APPL ISSUE FEE	$200.00	Deposit Account

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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/262,898	01/05/2021	10882803	INLX.0198U1/484809	3410

171052 7590 12/16/2020

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ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 0 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

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