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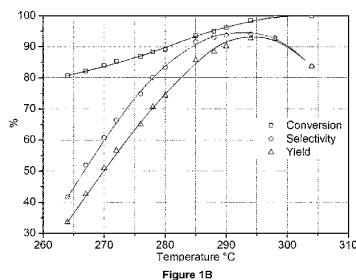
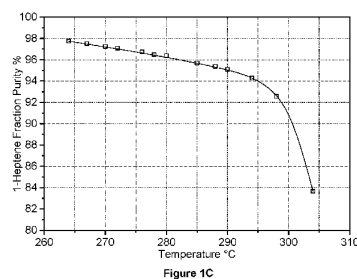
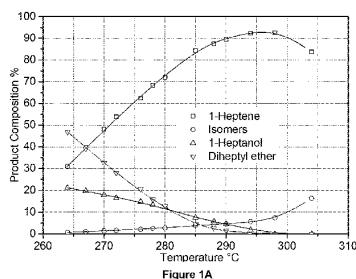
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(54) Title: PROCESS FOR THE EFFICIENT PREPARATION OF (BIO)-ALKANEDIOLS



(57) Abstract: The present invention relates to a process for the efficient, sustainable and gentle preparation of bio-based alkanediols, especially 1,2-alkanediols, at moderate temperatures based on a recycling of side products and non-reacted educts. The present invention also relates to a composition comprising at least two alkanediols obtainable by said process and to the use of said composition in consumer product formulations. In addition, the present invention relates to consumer products as such comprising the inventive composition.

[Continued on next page]

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Process for the efficient preparation of (bio)-alkanediols

Technical field

[0001] The present invention relates to a process for the efficient, sustainable, cost-effective and gentle preparation of (bio-based) alkanediols, in particular 1,2-alkanediols having 5 to 15 carbon atoms. The present invention also relates to a composition comprising at least two alkanediols preferably obtainable by said process and to the use of said composition in consumer product formulations. In addition, the present invention relates to consumer products as such comprising the inventive composition.

Background Art

[0002] It has been recently found that specific alkanediols, and in particular specific 1,2-alkanediols such as 1,2-hexanediol and 1,2-octanediol, can be advantageously added to a broad variety of consumer product formulations as multifunctional actives and during the last years several methods have been developed for the preparation of these substances.

[0003] Such alkanediols are usually prepared by hydrolysis of epoxyalkanes based on the epoxidation of olefins. However, often by-products are formed which are causing an unpleasant smell, which is why additional effort was made to improve said processes e.g. by additional purification methods.

[0004] For example, EP 1 876 162 A1 describes the preparation of alkanediol compounds having four or more carbon atoms from the corresponding olefins by means of epoxidation and subsequent hydrolysis followed by an additional treatment based on the addition of water and/or an organic solvent to the alkanediol composition and the subsequent removal of the water and/or the organic solvent under reduced pressure for purification and the removal of side products such as esters and dioxanes which might cause disadvantageous smells.

[0005] US 6,528,665 B1 proposes the preparation of pure alkanediols prepared from the corresponding epoxyalkanes, based on the epoxidation of olefinic compounds with hydrogen peroxide, subjecting the epoxyalkanes to a complex washing treatment using aqueous washing solutions of inorganic bases and borohydride, and subsequent hydrolyzation.

[0006] However, both processes require the use of additional chemicals and solvents as well as energy and generate a considerable amount of waste products. Consequently, these processes are neither ecologically nor economically efficient. In addition, both processes do not refer to the provision of the olefinic starting compounds.

[0007] EP 0 257 243 A1 discloses the preparation of low molecular weight vicinal diols by saponification of the corresponding epoxides with water by using specific epoxide to water ratios in the presence of a catalyst. A comparable process comprising reacting a 1-alkene with formic acid and hydrogen peroxide and subsequent saponification is disclosed in EP 0 141 775 A1 and requires several reaction stages connected in series. However, these processes have multiple economic and ecological disadvantages. For example, the diester of 1,2-pentanediol that is formed as an intermediate in the process must be saponified in order to obtain 1,2-pentanediol. If the epoxidation of n-pent-1-ene is carried out, for example, with hydrogen peroxide and formic acid, sodium formate is formed as a coupling product in the subsequent saponification of the diformate of 1,2-pentanediol with sodium hydroxide solution and must be disposed of, thus leading to a high load of organics in the waste water.

[0008] Another way to obtain alkanediols such as 1,2-pentanediol from renewable sources is described in WO 2019/152569 A2. WO 2019/152569 A2 discloses a process for converting an alkene to a 1,2-alkanediol, wherein the alkene is obtained by dehydrating a 1-alcohol in a reactor by heating in the presence of a specifically modified and high-temperature calcinated catalyst. Thereby, the process is based on a single pass of the gaseous reactants over the catalyst at high temperatures of approximately 315 °C. However, this process requires the application of high temperatures and additional steps for the complex catalyst preparation and

conversion of the alcohol to the alkene resulting in an economically and ecologically disadvantageous preparation process in conjunction with increased amounts of wastes produced upon catalyst preparation.

[0009] Therefore, none of the processes identified above provides for an economically and ecologically efficient and friendly method for the preparation of alkanediols, especially 1,2-alkanediols and the corresponding intermediate olefins. In particular, none of these processes allows for the economically and ecologically efficient preparation of 1,2-heptanediol, 1,2-octanediol and/or 1,2-nonanediol and the corresponding intermediate alkene compounds.

[0010] In addition, the desire for more sustainable preparation methods has increased over the past years and there is an ongoing need to improve the preparation of these valuable alkanediol compositions. Consequently, there is a high demand for fully efficient and sustainable preparation methods for these alkanediols as such.

[0011] It is therefore an object of the present invention to provide for a more sustainable, i.e. a more ecological and more economical process for the preparation of alkanediols having 5 to 15 carbon atoms using milder reaction conditions while simultaneously allowing for an improved balance of selectivity, yield and purity as well as a reduction of waste products, in particular in the preparation of the intermediate olefin compounds.

[0012] These and other objects and advantages of the present invention will become clear from the following disclosure.

[0013] Surprisingly, it has now been found in a first aspect that the process described herein allows for such an improved, sustainable and simultaneously efficient, preparation of high-purity alkanediols at moderate reaction conditions, in particular at moderate temperatures, allowing for the efficient preparation of alkanediols via the preparation of high-purity alkenes as intermediates. In addition, in total less process steps are required, no complex and costly modification of the

catalyst is necessary, and the overall costs and waste amounts are considerably reduced.

[0014] The present invention is specified in the appended claims. The invention itself, and its preferred variants, other objects and advantages, are however also apparent from the following detailed description in conjunction with the accompanying examples and figures.

Summary of the invention

[0015] In a first aspect, the present invention relates to a more ecological and economically more efficient process for the preparation of high-purity alkanediols having 5 to 15 carbon atoms, preferably 1,2-alkanediols, comprising the following steps:

- a) providing a 1-alcohol having 5 to 15 carbon atoms and/or a dialkylether having 10 to 30 carbon atoms and a catalyst;
- b) dehydrating the 1-alcohol and/or cleavage of the dialkylether to obtain at least one alkene having 5 to 15 carbon atoms, wherein the at least one alkene having 5 to 15 carbon atoms is at least one olefin selected from the group consisting of: α -, β - and/or γ -olefins each independently having 5 to 15 carbon atoms, preferably the at least one alkene is a α -olefin having a chain length of 5 to 15 carbon atoms;

wherein the dehydration and/or cleavage is performed with recirculation of dialkylether and 1-alcohol; and

wherein the dehydration and/or cleavage is performed at a temperature ranging from 255 °C to 290 °C;

- c) reaction of the at least one alkene to obtain a product comprising or consisting of at least one alkanediol having 5 to 15 carbon atoms, preferably the product is at least a 1,2-alkanediol.

[0016] In a preferred variant, the present invention relates to a process for the preparation of alkanediols having 5 to 15 carbon atoms, wherein in step c) of the process indicated above a product comprising or consisting of at least two alkanediols is obtained, wherein the at least two alkanediols are selected from the

group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms; wherein in the product, the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01.

[0017] This process allows for the preparation of alkanediols, and more specifically 1,2-alkanediols and/or specific alkanediol mixtures, having 5 to 15 carbon atoms using milder reaction conditions under reduced waste production in a more sustainable and economical manner, in particular during the preparation of the corresponding intermediate olefins according to step b) of the process. Based on the above sustainable process, it is possible to prepare highly pure (x,x+1)-alkanediols, preferably 1,2-alkanediols, or mixtures of (x,x+1)-alkanediols, while simultaneously allowing for a gentle process with considerably reduced waste production and costs.

[0018] In a second aspect, the present invention relates to a composition comprising or consisting of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms, wherein the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 90 : 10 to 99.9 : 0.1 and/or wherein the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01.

[0019] Preferably said composition is obtainable according to the process of the present invention.

[0020] In a further aspect, the present invention relates to the use of the composition according to the invention for the preparation of consumer products such as cosmetics, personal care products, in particular skin cleaning products, shampoos, rinse-off conditioners, deodorants, antiperspirants, body lotions, textile care products, household products, in particular liquid detergents, all-purpose cleaners, laundry and cleaning agents, fabric softeners, scent boosters, fragrance enhancers and pharmaceutical compositions as well as the consumer products as such comprising the composition according to the invention.

[0021] Surprisingly it has been found that the overall process according to the present invention allows for the economically and ecologically efficient preparation of highly valuable alkanediols, especially a 1,2-alkanediol-based product or a mixture of a 1,2-alkanediol and a 2,3-alkandiol and/or a 3,4-alkandiol and in particular the preparation of the corresponding intermediate olefin compounds in a step b), with a reduced number of total process steps at moderate temperatures and with commercially available catalysts while simultaneously the amount of waste production is considerably reduced and allowing for an ideal balance of selectivity, yield and purity. Consequently, the process according to the invention allows for a more sustainable preparation of the desired compounds or compositions.

Description of Figures

[0022] **Figures 1A to 1C:** Figures 1A to 1C show the experimental results of Experiment 1 in view of product composition (Figure 1A), conversion, selectivity, yield (Figure 1B) and purity (Figure 1C).

Detailed description of the invention

[0023] Primarily, the present invention relates to a process for the preparation of alkanediols having 5 to 15 carbon atoms.

[0024] The term “alkanediol” within the context of the present invention also includes its constitutional isomers or position isomers. Constitutional isomers are compounds that have the same molecular formula and different connectivity. Position isomers, a particular form of constitutional isomerism, are structural isomers that can be viewed as differing only in the position of a functional group on a parent structure, which in this case is the position of the two alcohol functions.

[0025] Depending on the number of the carbon atoms of the carbon chain of the alkanediol, there are various position isomers of the alkanediol: (x,x+1) constitutional isomers; (x,x+2) constitutional isomers; (x,x+3) constitutional isomers; etc., wherein x stands for the number of the carbon atom in the alkanediol chain to which the OH groups of the alkanediol are chemically bonded.

[0026] In the (x,x+1) constitutional isomers, the two OH functional alcohol groups are vicinally attached to two different adjacent carbon atoms in the chain. In the (x,x+2) constitutional isomers, the two OH functional groups are attached to two different carbon atoms in the chain where the two carbon atoms are separated by one C atom. In the (x,x+3) constitutional isomers, the two OH functional groups are attached to two different carbon atoms in the chain where the two carbon atoms are separated by two C atoms.

[0027] In a preferred variant, the alkanediols obtainable with the process according to the invention are linear alkanediols having a carbon chain of 5 to 15 carbon atoms, and are preferably vicinal (x,x+1) diols, selected from the group consisting of 1,2-diols, 2,3-diols and 3,4-diols or mixtures thereof.

[0028] Especially preferred, the main component of the product is a 1,2-alkanediol or a 1,2-alkanediol having as a minor component the respective 2,3- and/or 3,4-alkanediol analogues. Therefore, the present invention mainly focusses on the preparation of (x,x+1) alkanediols and specifically on the preparation of high purity 1,2-alkanediols or a mixture of a 1,2-alkanediol and a 2,3-alkandiol and/or a 3,4-alkandiol, which each and independently are preferably linear in nature and have a chain length of 5 to 15 carbon atoms.

[0029] More specifically, in a first aspect, the present invention relates to a process for the preparation of alkanediols having 5 to 15 carbon atoms, and preferably comprising or consisting of a 1,2-alkanediol or a mixture of a 1,2-alkanediol and a 2,3-alkanediol and/or a 3,4-alkanediol, comprising the following steps:

- a) providing a 1-alcohol having 5 to 15 carbon atoms and/or a dialkylether having 10 to 30 carbon atoms and a catalyst;
- b) dehydrating the 1-alcohol and/or cleavage of the dialkylether to obtain at least one alkene having 5 to 15 carbon atoms, wherein the at least one alkene having 5 to 15 carbon atoms is at least one olefin selected from the group consisting of: α -, β - and/or γ -olefins each independently having 5 to 15 carbon atoms, and preferably an α -olefin having a chain length of 5 to 15 carbon atoms;

wherein the dehydration and/or cleavage is performed with recirculation of dialkylether and 1-alcohol; and

wherein the dehydration and/or cleavage is performed at a temperature ranging from 255 °C to 290 °C;

c) reaction of the at least one alkene, preferably a α -olefin, to obtain a product comprising or consisting of at least one alkanediol having 5 to 15 carbon atoms, preferably a 1,2-alkanediol.

[0030] In a preferred variant the present invention relates to a process for the preparation of alkanediols having 5 to 15 carbon atoms, wherein in step c) of the process indicated above a product is obtained comprising or consisting of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms; wherein in the product, the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01.

[0031] The as-obtained product comprising 1,2-alkanediol or 1,2-alkanediol as main component in a mixture of alkanediols, and in particular the 1,2-heptanediol, 1,2-octanediol or 1,2-nonanediol-based product with optionally or preferably the corresponding 2,3-heptanediol, 2,3-octanediol or 2,3-nonanediol, is neutral in odor and obtained in liquid form allowing for the facilitated incorporation of said substances obtainable by said process into a variety of product formulations without negatively affecting the final product properties such as the odor. Correspondingly, the product obtained in step c) of the process according to the invention is a 1,2-alkanediol having 6 to 9 carbon atoms or a product comprising or consisting of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 7 to 9 carbon atoms.

[0032] In addition, it was observed, that the corresponding 2,3-alkanediols (and/or 3,4-alkanediols) as such are neutral in odor and obtainable in liquid form, likewise allowing for the advantageous incorporation into various product formulations.

[0033] The formation of side products such as esters and dioxanes which might cause disadvantageous smells was not observed when preparing alkanediols according to the process specified herein.

[0034] With the low temperature process according to the invention, it was possible to achieve high-quality alkanediols without the requirement of additional complicated purification processes.

[0035] The term “comprising” means that the named components are essential, but other components may be added and are still embraced by the present invention while the term “consisting of” as used according to the present invention means that the total amount of components adds up to 100 % by weight, based on the total weight of the corresponding product or composition, and signifies that the subject matter is closed-ended and can only include the limitations that are expressly recited. Whenever reference is made to “comprising” it is intended to cover both meanings as alternatives, that is the meaning can be either “comprising” or “consisting of”, unless the context dictates otherwise.

[0036] The terms “at least one” and “at least two” mean that the corresponding product or composition according to the present invention can comprise either one or two or a mixture of two or more of the corresponding components, respectively.

[0037] The composition obtainable in step c) of the process according to the invention comprises or consists of at least one alkanediol having 5 to 15 carbon atoms which is preferably a 1,2-alkanediol or a mixture of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms. If the desired product is a 1,2-alkanediol, relatively low portions of 2,3- and/or 3,4-alkanediols in the final product are preferred, corresponding to high-purity 1,2-alkanediols having 5 to 15 carbon atoms. Consequently, in step b) of the process according to the invention preferably high amounts of the corresponding α -olefins are formed while the amounts of the corresponding β - and/or γ -olefins in the intermediate product of step b) are low. Even more preferred, in such cases the only olefin formed in step b) of the process according to the invention is a α -olefin. Thus, preferably high purity α -olefins are

formed in step b) of the process according to the invention. For mixtures of at least two alkanediols as specified above, correspondingly the ratios of the components of the mixture are reflected in the corresponding olefin-compounds of step b) of the process.

[0038] Thereby, in the case of mixtures, the ratio of the 1,2-alkanediol to the 2,3-alkanediol obtained by the inventive process, and more specifically in step c) of said process, is in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01. Preferably, the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 95 : 5 to 99.9 : 0.1 and preferably from 97.5 : 2.5 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 95 : 5 to 99.99 : 0.01 and preferably from 97.5 : 2.5 to 99.99 : 0.01.

[0039] Thus, in a further preferred variant, the product of the process according to the invention comprises a mixture of a linear 1,2-alkanediol and a 2,3-alkanediol and/or a 3,4-alkanediol, with preferably only minor portions of 2,3- and/or 3,4-alkanediols in the ratios specified above or in another preferred variant the final product of step c) is a high-purity 1,2-alkanediol.

[0040] In a preferred variant of the present invention, the ratio of the 1,2-alkanediol and a 2,3-alkanediol and/or a 3,4-alkanediol is high, corresponding to a high chemical purity of the product, i.e. the 1,2-alkanediol. Preferably, the purity of the 1,2-alkanediol obtainable by the inventive process is 95 % or higher, preferably 96 % or higher, even more preferred 97 % or higher, especially preferred 98 % or higher and most preferred 99 % or higher. By additional distillation of the products easily product purities of up to 99.9 % can be achieved.

[0041] Based on the process according to the invention, it is possible to achieve high-purity 1,2-alkanediols or mixtures of 1,2-alkanediols with low amounts of 2,3-alkanediols and/or 3,4-alkanediols as side products, wherein the 2,3-alkanediols form the main portion of the side products, i.e. extremely low portions of 3,4-alkanediols are present in the final product. For special applications, it can also be favorable to have a certain amount of 2,3 and/or 3,4 components in the composition. Such

mixtures can have good skin spreading properties, possibly due to the more diverse spectrum of components which have a broader interaction with the other components in topical formulations.

[0042] The purity of the final alkanediol compound is essentially reflected in the purity of the intermediary prepared alkene compounds. Accordingly, in step b) of the inventive process, preferably high-purity 1-alkenes (α -olefins) are obtained with only minor amounts of 2- and/or 3-alkenes (β - and/or γ -olefins) in order to prepare high-purity 1,2-alkanediols. Preferably, only 1-alkenes are formed in step b) of the process according to the invention.

[0043] Accordingly, in a preferred variant wherein the product comprises at least two alkanediols the proportion of the 1-alkene to the 2-alkene at the end of step b) is preferably in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1-alkene to the 3-alkene is in the range of 90 : 10 to 99.99 : 0.01. Preferably, the ratio of the 1-alkene to the 2-alkene is in the range of 95 : 5 to 99.9 : 0.1 and preferably from 97.5 : 2.5 to 99.9 : 0.1 and/or the ratio of the 1-alkene to the 3-alkene is in the range of 95 : 5 to 99.99 : 0.01 and preferably from 97.5 : 2.5 to 99.99 : 0.01.

[0044] Furthermore, in a preferred variant the purity of the 1-alkene is preferably 95 % or higher and preferably 96 % or higher, even more preferred 97 % or higher, especially preferred 98 % or higher and most preferred 99 % or higher. Additionally, the purity of the 1-alkene can be further increased by standard distillation techniques if required up to purities of about 99.9 % allowing for the preparation of high-purity alkanediols, and preferably 1,2-alkanediols, in step c) according to the inventive process.

[0045] The process described herein is characterized in particular by its high efficiency, as the process in question is preferably a so-called "self-regulating" process in which in a preferred variant with recirculation, a steady state can be achieved. This process equilibrium can be positively influenced by optimization of the recirculation rate and the selected reaction temperature. Additional variations of the residence time above the catalyst can, for example, also influence the product formation. In particular, it has been observed that the recycling rate as well as the low

temperatures as described herein have a positive effect on the formation of 1,2-alkanediols as the main product. Recirculation rates of the 1-alcohol and dialkylether of approximately 40 % (+/- 10 %) and temperatures below 300 °C enable the efficient and economically as well as ecologically improved formation of high-purity 1,2-alkanediols or mixtures of 1,2-alkanediols with lower levels of 2,3- and/or 3,4-alkanediols.

[0046] Moreover, the alkanediols according to the invention having 5 to 15 carbon atoms are preferably selected from the group consisting of pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, dodecanediols, tridecanediols, tetradecanediols and pentadecanediols in the corresponding isomeric form as defined above.

[0047] In a preferred variant, however, the corresponding alkanediol is selected from the group consisting of hexanediol, heptanediol, octanediol and nonanediol. Therefore, in a preferred variant a process according to the first aspect for the preparation of alkanediols having 6 to 9 carbon atoms is disclosed.

[0048] Consequently, step c) of the process according to the first aspect relates to the reaction of at least one alkene to obtain a product comprising or consisting of at least one alkanediol having 6 to 9 carbon atoms or a mixture of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 6 to 9 carbon atoms in the corresponding ratios specified above.

[0049] However, in a still more preferred variant, the process as described herein relates to the preparation of alkanediols having 7 or 8 carbon atoms, and preferably 7 carbon atoms. Therefore, in a further preferred variant a product comprising or consisting of at least one alkanediol having 7 or 8 carbon atoms or a mixture of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 7 to 8 carbon atoms, and preferably 7 carbon atoms, is obtainable, i.e. a product comprising or consisting of at least one alkanediol being 1,2-heptanediol or 1,2-octanediol or a mixture of at least two alkanediols selected from the group consisting of: 1,2-heptanediol, 2,3-

heptanediol and 3,4-heptanediol and/or 1,2-octanediol, 2,3-octanediol and 3,4-octanediol, respectively, in the ratios specified above.

[0050] In a first step a) a 1-alcohol having 5 to 15 carbon atoms as well as a suitable catalyst are provided. Additionally, or optionally, a dialkylether having 10 to 30 carbon atoms is provided. Preferably, only a 1-alcohol having 5 to 15 carbon atoms as well as a suitable catalyst is provided as starting material.

[0051] The 1-alcohol is thereby influencing the chain length of the corresponding final alkanediols and is preferably linear in nature.

[0052] Preferred 1-alcohols used for the process according to the invention are therefore preferably linear, saturated 1-alkanols having 5 to 15 carbon atoms, preferably 6 to 9 carbon atoms and even more preferred 7 or 8 carbon atoms, such as 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol and 1-pentadecanol, wherein 1-hexanol, 1-heptanol, 1-octanol and 1-nonanol are preferred.

[0053] Preferred dialkylethers used for the process according to the invention are organic compounds that have an ether group as their functional group, i.e. an oxygen atom substituted with two alkyl radicals (R1-O-R2). The alkyl radical can be the same or different from each other resulting in either symmetrical dialkylethers or asymmetrical ones. Consequently, each alkyl radical has independently 5 to 15 carbon atoms corresponding to 10 to 30 carbon atoms in total. The use of symmetrical dialkylethers results in the formation of olefins all having the same chain length while dialkylethers having two different alkyl radicals cause the formation of olefins having different chain lengths corresponding to the chain lengths of the alkyl radicals of the dialkylether. Consequently, it is possible to obtain mixtures of olefins differing in chain length. A comparable effect can be achieved by providing a mixture of different 1-alcohols each differing in chain length. Thereby, the dialkylether provided in step a) is either freshly added dialkylether and/or dialkylether formed in step b) as intermediate itself in the formation of the intermediate olefin compounds for preparing the corresponding final alkanediol product in step c).

[0054] Suitable catalysts used for the process according to the present invention are preferably commercially available and are preferably alumina based. However, generally any suitable catalyst known in the art can be used in the dehydration step b) of the process according to the invention.

[0055] In addition, the catalyst used for the process according to the present invention is preferably unmodified, i.e. neither doped with metals such as zirconium, zinc or other metal atoms or other additives or acids and bases nor processed or treated in any other physical or chemical way prior to utilization.

[0056] Usually, the selectivity of a reaction can be increased by using doped or modified catalysts. However, due to a decrease in reactivity generally higher reaction temperatures are required. These high temperatures have a negative effect on the durability of the reaction equipment increasing wear of the equipment and resulting in additional costs for device inspections. Moreover, such high temperatures require expensive insulations rendering the equipment more expensive as such and temperatures above 300 °C are hard to achieve using oil-based heating so that very expensive liquid salt melts would have to be used for heating. In addition, such modifications are mostly rather complex and costly and cause additional chemical waste. Consequently, high temperatures are on the one hand economically inefficient and ecologically non-sustainable and on the other hand, if no specific catalyst is used, result in reduced product selectivity due to the formation of side products. However, the use of specifically modified catalysts requires additional reaction steps and often very high calcination temperatures so that these catalysts do not seem an appropriate solution.

[0057] However, it has now been found that commercially available non-modified catalysts can be used to achieve high-purity alkanediols or alkanediol mixtures as specified above at moderate reaction conditions based on the process according to the invention which itself is based on the recirculation of intermediary formed products and non-reacted educts. Therefore, the present invention preferably employs a non-modified catalyst.

[0058] Preferably, the non-modified catalyst used in the process according to the invention, is a catalyst consisting of alumina (Al_2O_3) such as high purity gamma ($\gamma\text{-Al}_2\text{O}_3$), transitional ($\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$) and alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) or $\eta\text{-Al}_2\text{O}_3$ in the form of powders, granules, spheres, high density pellets and the like. Preferably, the catalyst has a pore volume ranging from 0.2 to 1.5 ml/g and even more preferred from 0.35 to 1.0 ml/g. A catalyst having a surface area of 120 to 250 m^2/g and even more preferred of 130 to 225 m^2/g is also suitable.

[0059] Preferably, unmodified γ -alumina is used as the catalyst, which is commercially available and does not require additional modifications prior to use.

[0060] Therefore, according to a further preferred variant, a process for the preparation of alkanediols is disclosed, wherein in step a) the used catalyst is an unmodified γ -alumina-based catalyst.

[0061] It is therefore a further object of the present invention, to provide a process for preparing alkanediols, and preferably 1,2-alkanediols, and in particular the corresponding intermediary formed olefins by dehydration of alcohols and/or cleavage of dialkylether, which is more sustainable and has a good balance between yield, selectivity and purity and simultaneously a reduced waste production at moderate temperatures of less than 300 °C allowing for the ecologically-friendly and economically efficient preparation of the desired alkanediols, especially the 1,2-alkane products with high purities or alkanediol mixtures as specified herein. Thereby, preferably no additional modification of the catalyst is required.

[0062] Based on the gentle process and the recycling according to the invention, it is possible to reduce the amount of waste produced to a minimum, such as dialkylethers or non-reacted educts which would otherwise be lost to the production. Furthermore, other types of waste such as formed in exotic side-reactions such as carbon backbone rearrangements are highly suppressed in the present inventive process.

[0063] Presently, intermediary formed dialkylether and/or non-reacted dialkylether in the preparation of the corresponding alkenes are fully recycled and only extremely

low amounts of 2-alkenes (and consequently the corresponding 2,3-alkanediols) are formed. However, the present process allows for modest or even low 2-alkene formation and especially even lesser amounts of 3-alkenes and their formation. Thus, only extremely low amounts of 2-alkenes, and of 3-alkenes (and thus the corresponding 3,4-alkanediols), are obtained as side products. The only additional compound formed is water which can be recycled in other reactions or disposed without having any negative ecological or economic impact. Consequently, it is possible to decrease the amount of side-product formation and allow for the gentle and sustainable preparation of high-purity 1-alkenes and thus highly pure 1,2-alkanediols. Also, non-reacted alcohol and intermediary formed alcohol are fully consumed during recirculation.

[0064] Preferably, the amount of 2-alkanes and/or 3-alkanes or other positional isomers other than the 1-alkene is below 5 % by weight referring to the total alkene product, preferably less than 3 % by weight.

[0065] In addition, the mild reaction conditions allow for a considerable increase in catalyst service life, which underlines the advantages and sustainability of the process according to the invention in terms of ecological and economic aspects.

[0066] In a second step b) the 1-alcohol is dehydrated to obtain at least one alkene having 5 to 15 carbon atoms, preferably 6 to 9 carbon atoms and even more preferred 7 or 8 carbon atoms, and most preferred 7 carbon atoms, wherein the at least one alkene having 5 to 15 carbon atoms, and preferably 6 to 9 carbon atoms and even more preferred 7 or 8 carbon atoms, is at least one olefin, selected from the group consisting of: α -, β - and/or γ -olefins, preferably a α -olefin having the corresponding chain length. In order to prepare high purity 1,2-alkanediols, the as-obtained olefin is preferably a (high-purity) α -olefin. However, as indicated above, it is also possible to prepare a mixture of olefins varying in chain length. These different olefins themselves can be α -, β - and/or γ -olefins.

[0067] Additionally, or alternatively, in step a) dialkylether is cleaved to form the corresponding 1-alcohols and/or 1-alkenes.

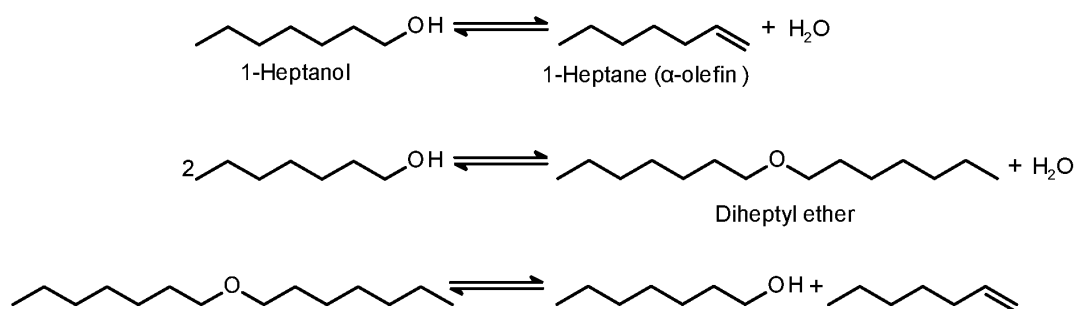
[0068] α -Olefins are alkenes having a double bond at the primary or alpha (α) position of the molecule (1-olefin/alkene). Accordingly, in a β -olefin the double bond is located between the second and third C-atom of the molecule (β -position: 2-olefin/alkene) while in γ -olefins the double bond is located between the third and fourth C-atom of the molecule (γ -position: 3-olefin/alkene).

[0069] The terms "olefin" and "alkene" are used synonymously. Also, the terms " α -olefin", " α -alkene", "1-olefin" and "1-alkene" are used synonymously. The same applies for the corresponding isomers " β -olefin", " β -alkene", "2-olefin" and "2-alkene" or " γ -olefin", " γ -alkene", "3-olefin" and "3-alkene".

[0070] As the product of the process according to the invention consist of or comprises a linear 1,2-alkanediol or a mixture of a linear 1,2-alkanediol and a 2,3-alkanediol and/or a 3,4-alkanediol in specific ratios wherein the content of the 2,3-alkanediol and/or the 3,4-alkanediol is low relative to the main product, i.e. the 1,2-alkanediol, the intermediate product of step b), i.e. the olefin compound can consist of or comprise a linear α -olefin or a mixture of a linear α -olefin with a β -olefin and/or a γ -olefin after the dehydration of the alcohol and/or cleavage of the dialkylether having the chain lengths specified above. Preferably, the as-obtained olefin is a high-purity α -olefin or a α -olefin with low β -olefin and/or γ -olefin contents in the specified ratios.

[0071] Therefore, in a preferred variant it is important to provide for a high-purity α -olefin having a chain length of 5 to 15 carbon atoms in step b) as intermediates in the preparation of high-purity 1,2-alkanediols having a chain length of 5 to 15 carbon atoms.

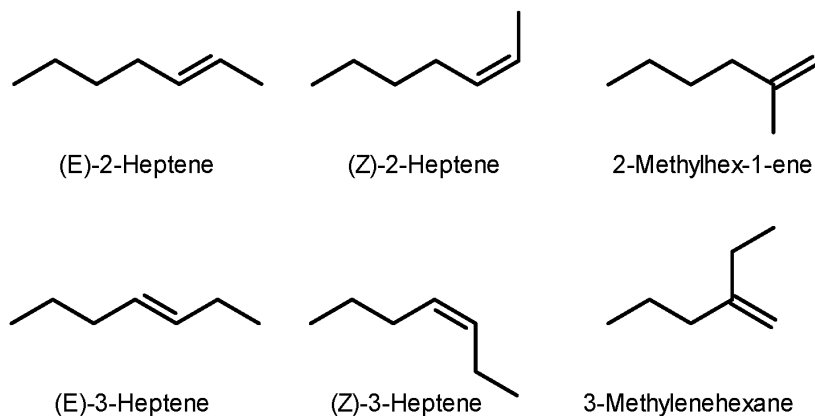
[0072] During the dehydration dialkylether might be formed and the product of step b) can additionally comprise unreacted educt, i.e. 1-alcohol or newly formed 1-alcohol based on the following reaction scheme originating from the cleavage of the dialkylether:



Reaction scheme (1): Dehydration of 1-alcohol to the corresponding alkene and side product formation

[0073] This alcohol can be recirculated together with the dialkylether formed in the process in order to efficiently reduce waste and simultaneously improve the balance of conversion efficiency, yield, purity and selectivity. Additionally, in cases wherein dialkylether is provided in step a) as starting material, step b) can also comprise non-reacted dialkylether, which is also recirculated. Therefore, in step b) dialkylether and 1-alcohol is recirculated.

[0074] Possible isomers of the intermediary formed 1-alkene according to the inventive process are exemplarily shown for 1-heptene in the following:



Structural isomers of 1-heptene

[0075] With the present approach, it is possible to achieve a specific and low amount of said olefins as side products and thus of the corresponding diols within the

final product, while allowing for a high yield of the particularly desired 1,2-alkanediols with excellent purity via the preparation of high quality α -olefins as intermediates in step b).

[0076] Thereby, the dehydration and/or cleavage according to step b) of the process according to the invention is performed with recirculation of said dialkylether as well as 1-alcohol as specified above. Overall, this allows for a more efficient and sustainable approach towards a more ecological and economical preparation of 1,2-alkanediols with increased yields and purities at moderate reaction conditions while simultaneously allowing for a considerable reduction in waste products and costs. In addition, additional costs for waste treatment are more or less minimized.

[0077] Thereby it is sufficient to perform the dehydration at moderate temperatures ranging from 255 °C to 290 °C and using commercially available catalyst systems in order to achieve an ideal balance between selectivity, yield and purity of the 1,2-alkanediols by simultaneously reducing the amount of waste products and the energy and costs required for the reaction and for waste disposal.

[0078] However, preferably in the process according to the invention, the dehydration of step b) is performed at a temperature ranging from 260 °C to 280 °C and even more preferred from 270 °C to 280 °C. If the dehydration of step b) is performed within this range, an ideal balance of yield, purity and selectivity at moderate reaction conditions could be achieved. The relatively low reaction temperatures allow for the efficient preparation of α -olefins and consequently of 1,2-alkanediols with lesser formation of β - and/or γ -olefins.

[0079] Advantageously, the dehydration is performed in a reactor with gaseous educts passing over the catalyst. Suitable reactors are for example fixed bed reactors, fluidized bed reactors, tubular reactors, and other suitable reactors allowing for intimate contact between the educt and the catalyst. Preferably, in the process according to the invention the reaction chamber used in step b), and in which the dehydration of the alcohols and/or cleavage of the dialkylether takes place, is a fixed bed reactor, preferably having at least one reaction zone equipped with a catalyst as specified above.

[0080] Preferably, the reaction chamber is a commercially available standard fixed-bed reactor as such a reactor is preferred due to its lower costs and facilitated handling. Alternatively, a so-called tube bundle reactor can be used.

[0081] In addition, the liquid hourly space velocity (LHSV) of the reactants over the catalyst within the reaction chamber for dehydration in step b) is preferably ranging from 0.5 to 10 1/h, even more preferred from 0.5 to 5 1/h or from 0.5 to 3.5 1/h, in order to achieve an efficient dehydration and/or cleavage. This allows for a mild conversion of the reactants due to reduced residence times of the reactants on the catalyst. This allows for an additional increase in the catalyst life cycle. If the LHSV of the reactants over the catalyst is within the ranges specified above, it is simultaneously possible to additionally reduce the formation of β - and/or γ -olefins and thus of side products.

[0082] It was surprisingly found, that it was possible to increase the purity and yield at moderate reaction conditions and achieve an ideal balance of yield, selectivity and purity in step b), and thus the overall product, by recirculating dialkylether and 1-alcohol back into the reaction chamber and over the catalyst simultaneously allowing for a considerable reduction of waste and the use of moderate temperatures, both being beneficial from an ecological and economical point of view.

[0083] In addition, the recirculation promotes a gentler preparation of the desired 1,2-alkanediols at moderate conditions. The use of a nonmodified catalyst usually results in a reduction of the product selectivity and thus reduced purities and yield while low temperatures likewise result in a decreased conversion of the educts and thus in reduced yields and purities of the intermediate olefin compounds of the overall process described herein. However, on the other hand, low temperatures reduce the probability of intramolecular rearrangements of the double bonds and consequently the formation of 2-alkenes and 3-alkenes and thus 2,3-alkanediols and 3,4-alkanediols allowing for a high 1,2-alkanediol to 2,3-alkanediol and/or 3,4-alkanediol ratio, i.e. high purity 1-alkenes and 1,2-alkanediols, respectively. However, it was found that the recirculation of non-reacted dialkylether or intermediary formed dialkylether and non-reacted 1-alcohol or 1-alcohol side products allows for an

improved balance between conversion, selectivity and yield, allowing for the ecological and efficient formation of 1-alkenes and 1,2-alkanediols with high purities, respectively.

[0084] Likewise, reduced residence times of the reactants at the catalyst cause lower conversion rates and thus yields, but on the other hand allow for a higher 1-alkene selectivity and purity. However, it was surprisingly found that the reduced conversion rates and yields can be efficiently compensated by recirculation in an eco-friendly manner at low costs.

[0085] Preferably, in the process according to the first aspect, the non-reacted or intermediary formed dialkylether and non-reacted and newly formed 1-alcohol are recirculated and combined with fresh educt, i.e. with fresh 1-alcohol and/or fresh dialkylether, preferably fresh 1-alcohol as explained above. Thereby, in a preferred variant in the recirculation, the ratio of freshly added 1-alcohol (i.e. alcohol that was not yet involved in the reaction) to the recycling compounds (i.e. non-reacted educt and dialkylether and alcohol formed in the preparation of the alkenes) ranges from 95 : 5 by volume (corresponding to low recycling rates, i.e. high amounts of fresh 1-alcohol are added) to 5 : 95 by volume (corresponding to high recycling rates, i.e. low amounts of fresh 1-alcohol are added). Preferably the ratio is between 80 : 20 and 20 : 80 in step b) of the process according to the invention. Preferably the ratio of the recycling compounds to the freshly added 1-alcohol is 30 : 70 to 50 : 50 by volume. This approach allows for an increased efficiency of the process and allows for the continuous preparation of the desired 1,2-alkanediol products via the preparation of high-quality α -olefins in a sustainable and gentle manner. Advantageously, the ratio of the recycling compounds to freshly added 1-alcohol is 40 (+/-10) : 60 (+/- 10) by volume corresponding to a recirculation rate of 40 % +/- 10 % by volume relative to the total volume of the recycling compounds and freshly added 1-alcohol. This recirculation rate is most preferred in order to achieve the ideal balance between conversion, selectivity, yield and purity taking ecological and economical aspects into account.

[0086] Optionally, dialkylether can be selected as the sole or additional starting educt. Additionally, the corresponding dialkylether can be the only substance recirculated, if it is separated from the other compounds before recirculation.

[0087] Therefore, in a preferred variant of the inventive process, the dehydration and/or cleavage of step b) is performed as a continuous steady-state process, wherein the intermediary formed side products in the preparation of the alkenes and nonreacted educts (i.e. the recycling compounds) are continuously recirculated after simple separation of aqueous components and the product. Optionally, it is possible to add a distillation step before the recirculation for additional purification of the olefin-products.

[0088] However, also batchwise preparations are suitable.

[0089] In any case, optionally the collected olefin-products can be subjected to an additional distillation treatment allowing for the isolation of high-purity olefins, preferably α -olefins having 5 to 15 carbon atoms reaching purities up to 99 % or higher and allowing for the preparation of high-purity 1,2-alkanediols without the compelling requirement of additional purification steps.

[0090] Thereby, preferably the gaseous educt, i.e. the 1-alkanol is passed through the reactor comprising the catalyst at an internal temperature of 255 °C to 290 °C and preferably 270 °C to 280 °C and thus less than 280 °C.

[0091] Generally, for the endothermic process described herein, the required energy can be provided by various process approaches: (i) by external heating of the reaction reactor (tube-bundle reactor) by using a heat transfer medium such as oil, an electrical source, or any other external heat source; (ii) by usage of an adiabatic fixed bed reactor using an internal heat transfer medium such as N₂ or a H₂O steam; and (iii) by usage of an adiabatic fixed bed reactor using a superheated alcohol (educt) steam in such a way, that the preferred reaction temperature is reached at the reactor outlet.

[0092] However, if the temperature for heating is in the range of 300 °C to 500 °C, high costs, an increase of the susceptibility to corrosion of the apparatus and an aggravation of the handling and control of the heat transfer media can be observed.

[0093] In addition, preferably a so-called purge gas is used which is usually an inert gas such as nitrogen. However, the use of such a gas is not decisive for the efficiency of the present invention and might be omitted. Generally, low amounts of purge gas are preferred. The use of such purge gas has a diluting effect, wherein an increase in dilution results in a deterioration of the LHSV, while low dilution rates equal better LHSV values. Consequently, a bigger cooling equipment would be required in order to collect the product of step b). Thus, alternatively, the process according to the invention can be performed without the use of gaseous N₂ at all.

[0094] If a purge gas is used, an additional dilution of the reactants can be achieved. By increasing the inert gas portion, the conversion efficiency can be increased while however, simultaneously resulting in a decreased α -olefin purity and thus in an increased portion of the β -olefins and/or γ -olefins in the product of step b). Therefore, rather low dilutions are preferred.

[0095] Subsequently, the as-obtained intermediate gaseous product of step b) comprising the alkenes, possibly non-reacted alkanol and/or dialkylether as well as intermediary formed dialkylether or other side products are condensed. After separation of the aqueous phase the organic phase is preferably distilled in order to separate the desired alkenes and the remaining distillation bottoms are recirculated into the reaction chamber, and combined with fresh educt, preferably fresh alcohol in the ratios specified above, for further reaction. Preferably, at the end of the process, the as-obtained alkene-products are purified by additional distillation treatment.

[0096] This process could also be implemented as continuous process.

[0097] Preferably, the recirculation rate (or recycle rate) of the organic bottoms (recycling compounds) comprising dialkylether and 1-alcohol relative to the total volume of the organic bottoms and freshly added 1-alcohol is in the range of 20 % to 80 % by volume and preferably 30 % to 50 % by volume. The recirculation rate as

used herein is defined as the ratio of the recirculated dialkylether and 1-alcohol to freshly added educt, i.e. 1-alcohol and/or dialkylether, but preferably 1-alcohol, by volume as indicated above. Most preferred, the recirculation rate is 40 % (+/- 10 %) by volume.

[0098] Thus, preferably, in each recycling cycle about 40 % (+/- 10 %) by volume of recycling compounds comprising dialkylether and 1-alcohol and about 60 % (+/- 10 %) by volume fresh 1-alcohol are fed into the reaction chamber. This corresponds to a recirculation rate of approximately 40 % (+/- 10 %) (i.e. a volume partition of 40 % (+/- 10 %) of the recirculated compounds by volume relative to the total dosage).

[0099] Based on the experiments, it can be assumed, without being bound to this assumption, that the organic bottoms comprise approximately 40 to 80 % by weight of dialkylether and 60 to 20 % by weight of 1-alcohol. As the process described herein is a self-regulated process, it follows that the more dialkylether is formed in step b), the more dialkylether is recirculated and vice versa. This assumes that water has been removed. If water is still present the above would be adapted accordingly.

[0100] The above preferred recirculation ratios allow for a further reduction of the reaction temperature required and thus for milder reaction conditions as such, resulting in a more gently process and reducing the ecological and economic impact of the preparation process when compared to state-of-the-art processes. Moreover, no complex and thus costly additional modification of the catalyst or waste disposal is required. Nevertheless, it is possible to achieve an excellent product purity based on an improved balance of yield, selectivity and conversion while simultaneously considering all ecological and economic aspects, in particular a considerably reduced waste production.

[0101] Thereby, surprisingly the overall conversion rate of the 1-alcohol can be increased up to 100 % in total. Surprisingly, it was possible to find the optimal process condition from an economical point of view allowing for an excellent balance between selectivity and recycling by selecting a recirculation rate of about 40 % (+/- 10 %) by volume and simultaneously allowing for excellent product purities. When using an unmodified Al_2O_3 catalyst without recirculation, only a poor alkene purity of

approximately 90 % would have been expected even at 100 % conversion, which is not sufficient for industrial applications. However, based on the inventive process it is possible to efficiently increase the product purity at high conversion rates through recycling.

[0102] However, also a comparable preparation of 1-alkenes based on the reaction of the corresponding dialkylether as only educt is possible, i.e. the reaction of pure dialkylether instead of the usage of alcohol compounds. In this case, the dialkylether is cleaved, in order to form an alcohol and the desired alkene compound. Subsequently, nonreacted ether, the formed alcohol and other by-products can be separated and optionally recirculated in order to achieve an ecological and economical process. Alternatively, a combination of 1-alcohol and dialkylether as educts can be used. However, preferably 1-alcohol is used as the educt.

[0103] Surprisingly, it was found that it is advantageous if the recirculation of the intermediate product is performed within the recirculation rates and temperature ranges specified above and that an highly efficient overall process especially in terms of costs, yield and product quality could be provided allowing for the ecologically and economically advantageous preparation of 1-alkenes and thus also 1,2-alkanediols with high purities. While it was possible to reduce the overall amount of waste products it was simultaneously possible to improve the balance of selectivity, purity and yield. Moreover, it is possible to achieve a high degree of alkene purity using commercially available catalysts and allowing for high catalyst service lives. Although the yield is decreasing due to the formation of dialkylether, this side product can be efficiently consumed and converted into high quality 1-alkenes at low temperatures by recirculation for the subsequent conversion into 1,2-alkanediols, preferably in form of a steady state process. Thereby, the overall waste product is minimized while simultaneously allowing for an excellent purity and consequently an improved balance between yield, purity and ecological and economical aspects.

[0104] Table 1 summarized the influence of the recirculation rate (recycling) of the distillation bottoms relative to the total feed as specified above on the conversion, selectivity, yield and α -olefin purity at moderate temperatures ($< 290\text{ }^{\circ}\text{C}$). The term "distillation bottoms" refers to the intermediary formed side products such as the

dialkylether or 1-alcohol and nonreacted educts which were separated from the product and aqueous components at the end of a reaction cycle by simple distillation and/or phase separation.

[0105] Table 1: Influence of the recirculation rate (recycling) in the conversion, selectivity, yield, and olefin purity (T = 274 °C +/- 8 °C).

Recycling [%]	20	40	60
Temperature [°C]	282	274	266
Conversion [%]	92	86	82
Selectivity [%]	87	71	49
Yield [%]	80	61	40
α -Olefin purity [%]	96.1	96.9	97.6

[0106] It is possible to obtain the primarily desired 1-alkenes in purities of at least 95 % and up to 98 % or higher. A recirculation rate of about 50 % as defined above results in a α -olefin purity of about 97 % or higher and a recirculation rate of about 60 % allows for the preparation of α -olefins having a purity of about 98 %. However, these conditions are not economic due to low yields and selectivities as well as due to high recirculation rates. After additional distillation purities of 99 % or higher can be achieved. Regarding an ideal balance between conversion, selectivity, yield and purity, a recycling rate of approximately 40 % (+/- 10%) by volume is preferred, e.g. optimizing the above, the recycling rate is preferably between 30 to 50 %, more preferably 40 % (+/- 10%) by volume.

[0107] In addition, it could be observed that the balance between dialkylether formation and cleavage can be controlled by the volume partition of the recirculated distillation bottoms added to the fresh feed of e.g. 1-alcohol (i.e. the recirculation rate), the reaction temperature, dilution with purge gas, i.e. an inert gas serving as heat transfer and/or transport medium and thus the residence time or flow of the reactants as well as the pressure.

[0108] The adjustment of these parameters as indicated above allows for improved 1-alcohol conversion as well as high 1-alkene purities at moderate reaction conditions and thus an ideal balance between conversion and purity for an economical, sustainable and gently process.

[0109] In a third step c) the at least one alkene obtained in step b), which is preferably a 1-alkene, is reacted to obtain a product comprising or consisting of at least one alkanediol having 5 to 15 carbon atoms or a mixture of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms as specified above, wherein in the product, the ratio of the 1,2-alkanol to the 2,3-alkanol is in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanol to the 3,4-alkanol is in the range of 90 : 10 to 99.99 : 0.01 as specified above.

[0110] The purity of the as-obtained 1,2-alkanediols is generally comparable to the purity of the intermediary formed olefin compound and is 95 % or higher, preferably 96 % or higher, even more preferred 97 % or higher, especially preferred 98 % or higher and most preferred 99 % or higher. By additional, distillation of the products easily product purities of up to 99.9 % can be achieved.

[0111] The reaction of the alkenes to the corresponding alkanediols is known to the person skilled in the art and is based on any suitable technique known in the art. Preferably, the alkene is converted into the corresponding alkanediol by reaction with formic or acetic acid in the presence of hydrogen peroxide, and further treatment with an aqueous base solution. Optionally, the as-obtained product is additionally distilled to further reduce the amounts of 2,3- and/or 3,4-alkanediols.

[0112] Therefore, in a preferred variant of the process according to the invention, step c) is accomplished by reacting the at least one alkene (and preferably the 1-alkene) with formic acid and peroxide followed by subsequent reaction with water and sodium hydroxide.

[0113] The alkenes obtained in step b) as well as the final alkanediols obtained in step c) of the inventive process each can be subject to an additional distillation step for further purification.

[0114] The purity of the as-obtained 1,2-alkanediols is 98 % or higher after distillation, even more preferred 99 % or higher. Alternatively, the ratio of the 1,2-alkanol to the 2,3-alkanol obtained by the inventive process, and more

specifically in step c) of said process, is in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01. Preferably, the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 95 : 5 to 99.9 : 0.1 and preferably from 97.5 : 2.5 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 95 : 5 to 99.99 : 0.01 and preferably from 97.5 : 2.5 to 99.99 : 0.01.

[0115] Therefore, in a preferred variant of the inventive process, the process additionally comprises at least one distillation step after step b) and/or step c).

[0116] Preferably, after both steps a distillation is performed. In addition, it is advantageous if the distillation apparatus used after step b) is directly connected to the reaction chamber to allow a continuous process.

[0117] For example, a phase separator can be connected to the reaction chamber to separate organic components from aqueous components obtained in step b). Thereby, the collected organic phase is cooled down. In a subsequent distillation step the desired alkenes can be isolated from the collected organic phase by heating. Thereafter, the remaining distillation bottoms are recirculated into the reaction chamber for further conversion into the desired alkenes. Consequently, this approach is particularly suitable for a batch-based process.

[0118] Alternatively, the reaction chamber is connected to a distillation apparatus allowing for the direct recirculation of the distillation bottoms, i.e. the recycling compounds to the reactor allowing for a continuous process.

[0119] In a second aspect the invention relates to a composition comprising at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms, preferably 6 to 9 and even more preferred 7 to 8 carbon atoms, and most preferred 7 carbon atoms, wherein the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 90 : 10 to 99.9 : 0.1 and/or wherein the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01 which is preferably obtainable through the process according to the invention.

[0120] Preferably, the portion of the 1,2-alkanediols to the 2,3-alkanediols and/or 3,4-alkanediols is as high as possible.

[0121] In addition, the composition can comprise a mixture of different alkanediols differing in chain length as specified above.

[0122] Another aspect of the invention relates to the use of the composition according to the invention for the preparation of a variety of consumer products such as cosmetics, personal care products, in particular skin cleaning products, shampoos, rinse-off conditioners, deodorants, antiperspirants, body lotions, textile care products, household products, in particular liquid detergents, all-purpose cleaners, laundry and cleaning agents, fabric softeners, scent boosters, fragrance enhancers and pharmaceutical compositions and the like.

[0123] Finally, another aspect relates to consumer products as such, such as cosmetics, personal care products, in particular skin cleaning products, shampoos, rinse-off conditioners, deodorants, antiperspirants, body lotions, textile care products, household products, in particular liquid detergents, all-purpose cleaners, laundry and cleaning agents, fabric softeners, scent boosters, fragrance enhancers and pharmaceutical compositions comprising the composition according to the invention.

[0124] However, the consumer product described herein may comprise the inventive composition, wherein alkanediols having different chain lengths may be present as well as other active ingredients.

Experimental

[0125] General procedure:

[0126] The following preparations of bio-alkanediols, especially 1,2-alkanediols and in particular 1,2-heptanediol, have been performed in a reactor which is made of a 100 cm long steel tube having an inner diameter of 14 mm. Heating was performed by an electrical heating mantle which has three temperature zones: a preheating zone being 30 cm in length which is filled with an inert carborundum filling; a subsequent 50 cm long zone forming the catalytic fixed-bed and consisting of solid catalyst particles being arranged as a so-called fixed bed in the reactor thus forming the reaction zone or reaction chamber; followed by a zone being 20 cm long filled with inert carborundum material (vertical arrangement from top to bottom). The three temperature zones are individually controlled. When reference is made to the temperature of the process, it is referred to the internal temperature in the middle zone forming the catalytic fixed-bed, i.e. the actual reaction zone where the dehydration and/or cleavage process takes place.

[0127] The catalyst bed is preheated and as soon as the desired temperature is reached the reactants are continuously pumped on top of the evaporation zone at rates of 0.5 ml/min - 10 ml/min and preferably 0.5 ml/min - 2.5 ml/min.

[0128] Liquid reagents are dosed with HPLC pumps and gaseous reagents are metered with the aid of mass flow controllers. Both, gaseous and liquid reagents, enter the reactor from the top of the vertical arrangement. The liquids flow along the first 30 cm of inert filling (preheating zone) due to gravity until complete evaporation. Progress is monitored by an internal temperature control. Thereby, the contact of the liquid with the catalyst filling should be avoided, as this could accelerate the deactivation of the catalyst.

[0129] The as-obtained gaseous educts enter the 50 cm catalyst zone. Due to the endothermic nature of the dehydration reaction a distinct temperature profile along the catalyst bed can be followed by an internal temperature control. In addition, a temperature profile across the catalyst bed might be observed, too.

[0130] Subsequently, the gaseous products pass the third zone with inert filling. Purpose of the last temperature zone is to avoid thermal loss and to achieve an isothermal reaction zone.

[0131] Finally, the gaseous products are condensed. Eventually non-condensable gaseous products are vented. The collected liquid products settle into an aqueous phase and an organic phase containing the desired alkenes which might be separated using simple phase separation methods known in the art. Simple distillation of the organic product phase finally yields the pure desired alkenes, preferably the 1-alkenes which are subsequently converted into 1,2-alkanediols according to step c) of the process. Additionally, the organic phase might be dried with a drying agent before distillation.

[0132] Subsequently, the as-obtained alkenes are converted to the corresponding alkanediols using common techniques.

[0133] Calculation of the 1-alkene fraction purity, conversion, selectivity and yield as well as liquid hourly space velocity:

[0134] In the following the term “heptene” refers to “1-heptene” while the term “isomers” refers to the structural isomers of the 1-heptene as exemplarily shown above and “heptanol” refers to “1-heptanol”.

[0135] The chemical purity of the 1-heptene fraction (relative to its mole number is defined as follows:

$$\text{Purity (heptene)} = \frac{\text{heptene}}{\text{heptene} + \text{isomers}}$$

Equation (1): Purity of 1-alkene

[0136] The molar conversion of the educt (i.e. 1-heptanol), selectivity and yield are defined as follows:

$$\text{Conversion} = \frac{2 \cdot \text{diheptyl ether} + \text{heptene} + \text{isomers}}{\text{heptanol} + 2 \cdot \text{diheptyl ether} + \text{heptene} + \text{isomers}}$$

Equation (2): Molar conversion rate of 1-alcohol (= ratio of how much 1-alcohol has reacted)

$$\text{Selectivity} = \frac{\text{heptene}}{2 \cdot \text{diheptyl ether} + \text{heptene} + \text{isomers}}$$

Equation (3): Molar selectivity (= ratio of how much 1-alkene was formed in ratio to the other products)

$$\text{Yield} = \frac{\text{heptene}}{\text{heptanol} + 2 \cdot \text{diheptyl ether} + \text{heptene} + \text{isomers}}$$

Equation (4): Molar yield (= ratio of how much 1-alkene was formed)

[0137] The liquid hourly space velocity (LHSV) is defined according to equation (5), wherein V(educt) represents the volumetric flow rate of the reactants entering the catalyst fixed bed and V(reactor) is defined as the volume of the catalyst fixed bed itself:

$$\text{LHSV} = \frac{\text{V(educt)}}{\text{V(reactor)} \cdot \text{time}}$$

Equation (5): LHSV

[0138] **Example 1:** Preparation of bio-alkenes based on the continuous addition of 1-alcohol – Temperature effect:

[0139] Bio-alkenes based on the continuous addition of pure 1-alcohol according to Example 1 were prepared as indicated above and based on the following reaction conditions:

1-Heptanol 2.5 ml/min

N₂ 8 ml_h/min
 Fixed-bed 14 mm ID x 500 mm (77.0 ml)
 Catalyst 63.0 g Alumina spheres (1.0 mm) from Sasol

[0140] Thereby nitrogen gas serves as carrier gas and optionally as heat transfer medium.

[0141] According to the product information the catalyst used in the experiment, Al₂O₃, has a packed bulk density of 740 to 820 g/l, a surface area ranging from 150 to 170 m²/g and a pore volume of at least 0.45 ml/g.

[0142] The catalyst bed was preheated and as soon as the desired temperature was reached 1-heptanol was continuously pumped on top of the evaporation zone at a rate of 2.5 ml/min. After two hours a steady state was achieved, and the corresponding temperature noted as well as a GC sample taken. Subsequently, the temperature was raised step by step as indicated in Table 2 and different curves showing the temperature dependence of the product composition, conversion, selectivity, yield and 1-heptene fraction purity are obtained (Figures 1A to 1C).

[0143] In this and the following examples the corresponding conversion rate, selectivity, yield and purity were calculated based on the equations specified above.

[0144] This example serves as control experiment.

[0145] Table 2 shows the corresponding product composition by weight in dependence of the temperature.

[0146] Table 2: Corresponding product composition by weight in dependence of the temperature.

Temp. [°C] Comp. [wt.-%]	264	267	270	272	276	278	280	285	288	290	294	298	304
1-Heptene	30.9	39.6	47.8	53.4	61.9	67.8	71.5	83.7	86.6	88.7	91.6	91.4	83.7
Heptene	0.7	1.0	1.4	1.6	2.1	2.5	2.7	3.8	4.2	4.6	5.6	7.3	16.3

Isomers													
1-Heptanol	21.1	19.6	17.8	16.4	14.7	13.2	12.3	7.4	5.8	4.4	1.7	0.0	0.0
Diheptyl Ether	46.6	39.0	32.4	27.8	20.4	15.7	12.7	4.3	2.5	1.5	0.2	0.0	0.0
Unknown	0.7	0.7	0.7	0.8	0.9	0.7	0.8	0.8	0.9	0.8	0.9	1.2	0.9
Conversion, selectivity, yield and purity of 1-heptene [%]													
Conversion	80.7	82.1	84.0	85.3	86.9	88.3	89.2	93.6	95.0	96.2	98.5	100	100
Selectivity	41.6	51.9	60.6	66.3	74.9	80.1	83.3	91.5	93.0	93.7	94.1	92.6	83.7
Yield	33.6	42.6	50.9	56.6	65.1	70.7	74.3	85.7	88.4	90.2	92.7	92.6	83.7
Purity	97.8	97.5	97.2	97.1	96.7	96.4	96.4	95.7	95.4	95.1	94.2	92.6	83.7

[0147] At temperatures of 298 °C and higher a complete conversion of 1-heptanol is achieved. At 298 °C, however, the purity of 1-heptene is only 91.1 %, which is too low for industrial applications. On the other hand, the 1-heptene purity at 280 °C is excellent (96.4 %), but the 1-heptene yield reaches only 74.3 %, which is due to high selectivity losses caused by the formation of diheptyl ether as a by-product according to the reaction scheme shown above. Such a yield is too low for industrial application. Therefore, there is great interest in creating added value from the by-product diheptyl ether, which is demonstrated by the following examples.

[0148] Moreover, it can be concluded that full conversion does not result in the required and thus desired purities of the α -olefin. In addition, it can be observed that an increase in temperature results in a decrease of the α -olefin purity, especially for temperatures higher than 290 °C.

[0149] **Example 2:** Preparation of bio-alkenes based on the continuous addition of 1-alcohol and diheptyl ether – Influence of the diheptyl ether dosage:

[0150] Bio-alkenes based on the continuous addition of pure 1-alcohol and diheptyl ether according to Example 2 were prepared as indicated above and based on the following reaction conditions:

Dosage	2.5 ml/min (sum of 1-heptanol and diheptyl ether)
N ₂	8 ml _N /min
Fixed-bed	14 mm ID x 500 mm (77.0 ml)
Catalyst	63.0 g Alumina spheres (1.0 mm) from Sasol

[0151] The catalyst bed was preheated and as soon as the desired temperature was reached 1-heptanol was continuously pumped on top of the evaporation zone at a rate of 2.5 ml/min. After two hours steady state was achieved, and a GC sample taken. In the same way an increasing share of diheptyl ether was dosed while keeping the total volume flow constant at 2.5 ml/min.

[0152] At 20 °C 1-heptanol has a density of 0.819 g/ml and diheptyl ether has a density of 0.801 g/ml. Considering these small differences in density 10 % by volume correspond to 9.8 % by weight of diheptyl ether and 20 % by volume corresponding to 19.6 % by weight of diheptyl ether.

[0153] Table 3 shows the corresponding product composition by weight in dependence of the temperature and diheptyl ether dosage (proof-of-concept).

[0154] Table 3: Corresponding product composition by weight in dependence of the temperature and diheptyl ether dosage.

Diheptyl Ether Dosage [vol.-%]	0	0	10	10	20	20
Increasing diheptyl ether dosage →						
Temp. [°C]	273	283	273	283	273	283
Comp. [wt.-%]						
1-Heptene	56.7	80.0	56.3	76.3	63.3	80.4
Heptene Isomers	1.8	3.5	1.8	3.0	2.1	3.4
1-Heptanol	16.1	9.5	15.8	10.8	13.9	8.9
Diheptyl Ether	24.7	7.0	26.2	9.8	20.6	7.2
Unknown	0.8	0.8	1.5	0.7	0.9	0.7
Water	11.4	13.7	10.6	12.6	10.6	12.3
Conversion [%]	85.6	91.8	86.0	90.7	87.8	92.4
Selectivity [%]	70.0	89.0	68.6	86.5	75.1	88.9
Yield [%]	59.9	81.7	59.0	78.4	65.9	82.1
Purity [%]	97.0	95.8	97.0	96.2	96.7	95.9

[0155] This example demonstrates that by small variation of the reaction temperature it is possible to find conditions at which either more diheptyl ether is formed or at which diheptyl ether is cleaved into additional 1-heptene value product. However, if solely 1-heptanol is used as feed always some diheptyl ether is formed

as by-product. This means that diheptyl ether recirculation is mandatory to achieve an economically feasible process and to reduce the overall amount of waste products.

[0156] As expected, increasing diheptyl ether partition, i.e. an increasing relative diheptyl ether dosage is resulting in a reduced formation of reaction water.

[0157] In addition, it can be concluded that at 273 °C more diheptyl ether is formed than added, while at higher temperatures (283 °C) more diheptyl ether is consumed than was initially added.

[0158] Moreover, it is expected that the same effect can be observed when the dosing speed and thus the residence time of the reactants over the catalyst is varied.

[0159] **Example 3:** Preparation of bio-alkenes based on the continuous addition of 1-alcohol and dilution with nitrogen gas – Influence of the dilution of the reactants:

[0160] Bio-alkenes based on the continuous addition of pure 1-alcohol according to Example 3 were prepared as indicated above and based on the following reaction conditions and under increasing dilution with gaseous nitrogen:

Fixed-bed 14 mm ID x 500 mm (77.0 ml)

Catalyst 63.0 g Alumina spheres (1.0 mm) from Sasol

[0161] So far as standard conditions a 1-heptanol flow of 2.5 ml/min (17.62 mmol/min) and a N₂ flow of 8 ml_N/min (0.35 mmol/min) were chosen. Such small amounts of N₂ inert gas were only used to avoid a back mixing of small amounts of O₂ in the reaction zone by diffusion during the reaction and to avoid flooding of the still hot reaction zone while cooling down the reactor.

[0162] However, larger amounts of an inert gas such as N₂ may be used as diluent and heat transfer medium. Since the dehydration takes place with an increase in the mole number, a constant total flow for 1-heptanol, H₂O and N₂ of 35.61 mmol/min was calculated. This is based on the described standard conditions that sum up to 2

times 17.62 mmol/min of 1-heptanol plus 0.35 mmol/min N₂. This ensures that the residence time of the reactants over the catalyst is kept constant and that only the N₂ inert gas dilution is varied during the experiment.

[0163] The temperature in all experiments according to Example 3 was kept constant at approximately 278 °C (+/- 4 °C).

[0164] Table 4 shows the corresponding product composition by weight in dependence of the dilution with gaseous N₂.

[0165] Table 4: Corresponding product composition by weight in dependence of the dilution with gaseous N₂.

1-Heptanol [ml/min]	2.50	2.17	1.68	1.01
N ₂ [ml _n /min]	8	114	266	479
N ₂ [mol.-%]	2	25	50	75
Increasing dilution of the reactants with N ₂ →				
Temp. [°C]	276	276	278	282
Comp. [wt.-%]				
1-Heptene	61.9	77.7	92.0	86.0
Heptene Isomers	2.1	3.2	5.6	13.0
1-Heptanol	14.7	9.9	1.5	0.0
Diheptyl Ether	20.4	8.4	0.2	0.1
Unknown	0.9	0.7	0.7	0.9
Conversion [%]	86.9	91.3	98.8	100
Selectivity [%]	74.9	87.7	94.1	86.8
Yield [%]	65.1	80.1	92.9	86.8
Purity [%]	96.7	96.0	94.3	86.9

[0166] These results show that an increasing portion of N₂ inert gas dilution is leading to higher conversion rates, but simultaneously to decreasing 1-heptene purities. In addition, it was shown that gaseous N₂ can suitably be used as internal heat transfer medium for adiabatic process alternatives.

[0167] Furthermore, it was observed that the dilution rate influences the formation of dialkylether. However, as indicated above, simultaneously the purity of the product decreases and an increased portion of the isomeric forms of the alkene are formed.

[0168] In aiming to reduce the content of isomeric forms, however, lower dilution rates are preferred allowing for the preparation of high quality 1-alkenes and thus the corresponding 1,2-alkanediols. It was now found, that the reduced yield can be efficiently compensated by a recycling process as specified herein allowing for an improved balance of yield and purity while simultaneously reducing the overall amount of waste products. Consequently, in the following examples according to the invention preferably a low portion of N₂ is chosen corresponding to a low dilution.

[0169] In addition, it is expected that a pressure variation should have the same effect as the dilution with inert gas.

[0170] **Example 4:** Preparation of bio-alkenes based on the partial conversion of 1-alcohol – Influence of partial conversion:

[0171] Bio-alkenes based on the partial conversion of 1-alcohol according to Example 4 were prepared as indicated above and based on the following reaction conditions:

1-Heptanol	2.5 ml/min
N ₂	8 ml _N /min
Fixed-bed	14 mm ID x 500 mm (77.0 ml)
Catalyst	63.0 g Alumina spheres (1.0 mm) from Sasol

[0172] The catalyst bed was preheated and as soon as the desired temperature was reached 1-heptanol was continuously pumped on top of the evaporation zone at a rate of 2.5 ml/min. After one hour a steady state was achieved with a temperature of 275 °C inside the catalyst bed. Thereafter, 2906.3 g 1-heptanol were added and 2893.8 g of the product collected within 24 hours. From the as-obtained product 353.8 g of a water layer were separated and the remaining 2539.0 g organic phase purified by distillation at 450 mmbar using a short 30 cm packed column equipped with a column head.

[0173] In summary, the mass reaction balance was as follows:

Water:	353.8 g
1-Heptene, pure:	1511.5 g
1-Heptene for re-distillation:	129.6 g (middle run fraction)
Distillation bottoms:	878.1 g
Loss:	19.8 g
Σ g	2892.8 g

[0174] Table 5 shows the corresponding composition of the as-obtained product after removal of water, the isolated 1-heptene product, the composition of 1-heptene obtained in a distillation middle run fraction which is to be re-distilled (to avoid waste and product losses) and finally the composition of the remaining distillation bottoms after removal of the 1-heptene product.

[0175] Table 5: Corresponding product composition by weight.

Compound [wt.-%]	Product as-obtained	Isolated 1-Heptene	1-Heptene for re-distillation (middle run fraction)	Remaining bottoms available for recirculation
1-Heptene	61.0	96.5	90.6	0
Heptene Isomers	2.2	3.4	5.8	0
1-Heptanol	15.2	0	1.3	42.8
Diheptyl Ether	20.8	0	0.2	55.5
Unknown	0.7	0.1	2.0	1.7
Compound [g]				
1-Heptene	1548.8	1458.7	117.4	0
Heptene Isomers	57.0	50.8	7.5	0.2
1-Heptanol	386.0	0.3	1.7	376.0
Diheptyl Ether	529.2	0.3	0.3	486.9
Unknown	17.9	1.4	2.6	14.7
Σ [g]	2539.0	1511.5	129.6	878.1
Conversion [%]	86.5	-	-	-
Selectivity [%]	74.1	-	-	-
Yield [%]	64.1	-	-	-
Purity [%]	96.4	96.6	94.0	-

[0176] The GC product analysis indicates 86.5 % of 1-heptanol conversion, 74.1 % 1-heptene selectivity and 64.1 % 1-heptene yield. Losses can be mainly attributed to the formation of diheptyl ether and to the less extend formation of heptene isomers. Surprisingly, a simple distillation is already leading to 1511.5 g of a 1-heptene fraction having an excellent purity of 96.4 %. Referring to a 2906.3 g (25.011 mol) 1-

heptanol feed this corresponds to an isolated yield of 1-heptene of 59.4 % (14.856 mol).

[0177] In addition, 129.6 g of a small middle run fraction containing further 4.8 % of additional 1-heptene (1.196 mol) crude yield for further isolation via re-distillation were obtained. The 878.1 g distillation bottoms contain mainly unwanted diheptyl ether by-product and to less extend unconverted 1-heptanol. This means than an 18.2 % diheptyl ether (2.271 mol) crude yield was obtained. However, 353.8 g (19.639 mol) of water were formed corresponding to a yield of 78.5 %.

[0178] **Example 5:** Preparation of bio-alkenes based on the continuous addition of 1-alcohol and distillation bottoms – Recycling process according to the invention:

[0179] Bio-alkenes based on the dehydration of 1-alcohol according to Example 5 were prepared as indicated above and based on the continuous addition of 1-alcohol and distillation bottoms (recycling process according to the invention) and the following reaction conditions:

Distillation Bottoms 42.8 % 1-heptanol, 55.5 % diheptyl ether and 1.7 % of unknown residues (see Example 4)

Dosage	2.5 ml/min of 1-heptanol and distillation residues/bottoms in total
N ₂	8 ml _n /min
Fixed-bed	14 mm ID x 500 mm (77.0 ml)
Catalyst	63.0 g Alumina spheres (1.0 mm) from Sasol

[0180] The catalyst bed was preheated and as soon as the desired temperature was reached, fresh 1-heptanol was continuously pumped on top of the evaporation zone at a rate of 2.5 ml/min. After two hours a steady state was reached, and a GC sample collected. In the same way, an increasing share of distillation bottoms (from Example 4) was dosed while keeping the total volume flow constant at 2.5 ml/min.

[0181] At 20 °C 1-heptanol has a density of 0.819 g/ml and the density of the distillation bottoms was 0.809 g/ml. For reference, 10 % by volume distillation bottoms correspond to 5.6 % by weight of diheptyl ether (corresponding to a

recirculation rate of 10 %) while 20 % by volume distillation bottoms correspond to 11.2 % by weight of diheptyl ether (corresponding to a recirculation rate of 20 %) and 30 % by volume distillation bottoms correspond to 16.8 % by weight of diheptyl ether (corresponding to a recirculation rate of 30 %), 40 % correspond to 22.4 % by weight of diheptyl ether (corresponding to a recirculation rate of 40 %) and 50 % correspond to 28.1 % by weight of diheptyl ether (corresponding to a recirculation rate of 50 %).

[0182] The temperature in all experiments according to Example 5 with increasing dosage of recirculation bottoms was kept constant at approximately 275 °C (+/- 2 °C).

[0183] Table 6 shows the corresponding product composition by weight in dependence of the addition of distillation bottoms.

[0184] Table 6: Corresponding product composition by weight in dependence of the addition of distillation bottoms.

Distillation Bottoms Dosage [vol.-%]	0	10	20	30	40	50
Temp. [°C]	274	275	275	276	276	277
Comp. [wt.-%]						
1-Heptene	66.9	63.6	61.1	60.4	58.7	57.2
Heptene Isomers	2.6	2.2	2.0	2.0	2.0	1.9
1-Heptanol	14.1	14.4	14.7	14.1	14.2	13.6
Diheptyl Ether	15.8	18.9	21.3	22.2	23.8	25.9
Unknown	0.6	0.8	1.0	1.4	1.2	1.5
Water	12.4	11.7	11.0	10.6	10.0	9.5
Conversion [%]	87.5	87.3	86.9	87.4	87.3	87.8
Selectivity [%]	79.7	76.5	74.0	73.0	71.1	69.1
Yield [%]	69.8	66.7	64.3	63.8	62.1	60.7
Purity [%]	96.3	96.6	96.8	96.8	96.7	96.8

[0185] This example demonstrates that by increasing the dosage of the distillation bottoms a certain point is achieved at which more diheptyl ether is cleaved than formed. This point is reached at a dosage of 40 to 50 % by volume of distillation bottoms (corresponding to a recirculation rate between 40 % and 50 % by volume as specified above). If the formed reaction water is taken into account, it can be concluded that this point is located between a dosage of 30 % to 40 % by volume of distillation bottoms, i.e. a recirculation rate of 30 to 40 % by volume. Accordingly, a dosage of 30 % to 40 % by volume of distillation bottoms is advantageous for a

waste reduced production process with high conversion rates and excellent product purities.

[0186] It should be noted, that in this example the distillation bottoms were not additionally purified before recycling.

[0187] Nevertheless, it was possible to obtain the desired 1-alkene, i.e. 1-heptene, having a high chemical purity.

[0188] In addition, it was observed that recycling of distillation bottoms allows for a further decrease of the required temperature to temperatures below 280 °C and approximately to 275 °C based on the reaction of the dialkylether to the corresponding 1-alcohol and 1-alkene. Comparably low reaction temperatures for the efficient preparation of 1-alkenes are not known from the state of the art.

[0189] This allows for mild reaction conditions, which allows for the further reduction of costs and increased equipment lifetimes. Based on the low temperatures in conjunction with the recycling an excellent balance between purity, yield and selectivity could be achieved, while simultaneous allowing for a considerable reduction in waste.

[0190] Moreover, this approach can efficiently be transferred to the industrial large-scale preparation of 1-alkenes and therefore the corresponding 1,2-alkanediols, especially from an ecological and economical point of view.

[0191] **Example 6:** Preparation of bio-alkenes based on the continuous addition of 1-alcohol and distillation bottoms – Recycling process according to the invention:

[0192] Bio-alkenes based on the dehydration of 1-alcohol according to Example 6 were prepared as indicated above and based on the continuous addition of 1-alcohol and distillation bottoms (recycling process according to the invention) and the following reaction conditions:

Distillation Bottoms 42.8 % 1-heptanol, 55.5 % diheptyl ether and 1.7 % of unknown residues

Dosage	0.5 ml/min
1-Heptanol	2.0 ml/min
N ₂	8 ml _h /min
Fixed-bed	14 mm ID x 500 mm (77.0 ml)
Catalyst	63.0 g Alumina spheres (1.0 mm) from Sasol

[0193] The catalyst bed was preheated and as soon as the desired temperature was reached, fresh 1-heptanol is pumped at a rate of 2.0 ml/min and distillation bottoms comprising diheptyl ether and 1-heptanol were pumped at a rate of 0.5 ml/min on top of the evaporation zone (corresponding to approximately 20 % recirculation, i.e. a volume partition of 20 % of the bottoms/recycling compounds relative to the total dosage). After one hour a steady state was reached with a temperature of 276 °C inside the catalyst bed. Subsequently, within 48 hours, 4717.4 g of 1-heptanol and 1164.7 g of distillation bottoms were dosed, and 5812.0 g of the as-obtained product collected. From the product 635.0 g of a water layer were separated and the remaining 5177.0 g of organic phase were purified by distillation at 450 mmbar using a short 30 cm packed column equipped with a column head.

[0194] In summary, the mass reaction balance was as follows:

Water:	635.0 g
1-Heptene, pure:	2925.7 g
1-Heptene, for re-distillation:	244.9 g (middle run fraction)
Distillation bottoms:	1982.7 g
Loss:	23.7 g
Σ g	5812.0 g

[0195] Table 7 shows the corresponding composition of the as-obtained product after removal of water, the isolated 1-heptene product, the 1-heptene obtained in an middle distillation run fraction which is to be re-distillated (to avoid waste and product losses) and finally the composition of the remaining distillation bottoms after removal of the 1-heptene.

[0196] Table 7: Corresponding product composition by weight.

Compound [wt.-%]	Product as-obtained	Isolated 1-Heptene	1-Heptene for re-distillation (middle run fraction)	Remaining bottoms for recirculation
1-Heptene	59.2	96.4	89.6	0
Heptene Isomers	2.1	3.1	4.8	0
1-Heptanol	14.6	0.1	1.9	37.6
Diheptyl Ether	23.2	0.2	0.2	60.1
Unknown	0.9	0.2	3.3	2.2
Compound [g]				
1-Heptene	3066.0	2819.7	219.4	0
Heptene Isomers	106.6	89.4	11.8	0
1-Heptanol	754.5	3.1	4.7	746.2
Diheptyl Ether	1201.6	7.3	0.6	1192.1
Unknown	47.9	6.1	8.2	43.4
Σ [g]	5177.0	2925.7	244.9	1982.7
Conversion [%]	87.0	-	-	-
Selectivity [%]	71.7	-	-	-
Yield [%]	62.4	-	-	-
Purity [%]	96.6	96.9	94.9	-

[0197] A GC measurement of the educts shows a conversion of 9.3 % due to the diheptyl ether content contained in the distillation bottoms. In total 5375.0 g of 1-heptanol and 507.1 g of diheptyl ether are dosed corresponding to a diheptyl ether content of 8.6 %.

[0198] A GC analysis of the products indicates a 1-heptanol conversion of 87.0 %, a 1-heptene selectivity of 71.7 % and a 1-heptene yield of 62.4 %. Losses can be mainly attributed to unreacted diheptyl ether and to a less pronounced formation of heptene isomers.

[0199] Surprisingly, a simple distillation is resulting in 2925.7 g of a 1-heptene fraction having an excellent purity of 96.4 %. Referring to the total feed this corresponds to an isolated 1-heptene yield of 56.3 % (28.724 mol). In addition, a small (244.9 g) middle run fraction contained further 4.4 % of crude 1-heptene yield (2.234 mol) for further isolation via re-distillation.

[0200] The 1982.7 g distillation bottoms contain mainly unwanted diheptyl ether by-product and to less extend unconverted 1-heptanol. This means 21.8 % of diheptyl

ether (5.560 mol) crude yield available for recycling is obtained. However, 635.0 g (35.248 mol) of the water formed correspond to a yield of 72.5 %.

[0201] **Example 7:** Preparation of bio-alkenes based on the continuous addition of 1-alcohol and distillation bottoms – Recycling process according to the invention:

[0202] Bio-alkenes based on the dehydration of 1-alcohol according to Example 7 were prepared as indicated above and based on the continuous addition of 1-alcohol and distillation bottoms (recycling process according to the invention) and the following reaction conditions:

Distillation Bottoms	44.2 % 1-heptanol, 55.1 % diheptyl Ether and 0.7 % of unknown residues
Dosage	1.0 ml/min
1-Heptanol	1.5 ml/min
N ₂	8 ml _n /min
Fixed-bed	14 mm ID x 500 mm (77.0 ml)
Catalyst	61.5 g Alumina spheres (1.0 mm) from Sasol

[0203] The catalyst bed was preheated and as soon as the desired temperature was reached, fresh 1-heptanol was pumped at a rate of 1.5 ml/min and distillation bottoms comprising diheptyl ether and 1-heptanol were pumped at rate of 1.0 ml/min on top of the evaporation zone (corresponding to approximately 40 % recirculation, i.e. a volume partition of 40 % of the bottoms relative to the total dosage). After one hour a steady state was reached with a temperature of 276 °C inside the catalyst bed. Subsequently, within 30 hours 2211.3 g of 1-heptanol and 1456.2 g of distillation bottoms were dosed, and 3589.0 g of the product collected. From the as-obtained product 360.3 g of water were separated and the remaining 3228.7 g of organic phase purified by distillation at 450 mbar using a short 30 cm packed column equipped with a column head.

[0204] In summary, the mass reaction balance was as follows:

Water:	360.3 g
1-Heptene, pure:	1944.0 g

1-Heptene, for re-distillation:	244.9 g (optional middle run fraction)
Distillation bottoms:	1269.0 g
Loss:	15.7 g
Σ g	3589.0 g

[0205] Table 8 shows the corresponding product composition of the as-obtained product after removal of water, the isolated 1-heptene product and the remaining distillation bottoms after removal of the 1-heptene.

[0206] Table 8: Corresponding product composition by weight.

Compound [wt.-%]	Product as-obtained	Isolated 1-Heptene	Bottoms for recirculation
1-Heptene	59.0	96.1	1.0
Heptene Isomers	1.9	3.2	0.1
1-Heptanol	15.2	0.4	38.0
Diheptyl Ether	22.9	0.0	58.8
Unknown	1.0	0.2	2.0
Compound [g]			
1-Heptene	1906.2	1868.8	13.2
Heptene Isomers	61.7	62.7	0.8
1-Heptanol	489.7	7.8	482.3
Diheptyl Ether	739.6	0.5	746.8
Unknown	31.5	4.2	25.8
Σ [g]	3228.7	1944.0	1269.0
Conversion [%]	86.5	-	-
Selectivity [%]	72.1	-	-
Yield [%]	62.3	-	-
Purity [%]	96.9	96.8	94.7

[0207] A GC analysis of the educt composition indicates a conversion of 23.4 % due to the high diheptyl ether content within the distillation bottoms. In total 2859.5 g 1-heptanol and 808.0 g diheptyl ether are dosed, corresponding to a diheptyl ether content of 22.0 %.

[0208] GC product analysis indicates a 1-heptanol conversion of 86.5 %, a 1-heptene selectivity of 72.1 % and a 1-heptene yield of 62.3 %. Losses can be mainly attributed to unreacted diheptyl ether and to less a less pronounced formation of heptene isomers.

[0209] Surprisingly, simple distillation is resulting in 1944.0 g of a 1-heptene fraction having an excellent purity of 96.4 %. Referring to the total feed this corresponds to an isolated 1-heptene yield of 59.4 % (19.086 mol).

[0210] The 1269.0 g distillation bottoms contain mainly the unwanted diheptyl ether by-product and to less extend unconverted 1-heptanol. This means that 21.7 % of a diheptyl ether (3.483 mol) crude yield were obtained. This example clearly demonstrates that under suitable conditions the product contains less diheptyl ether than the educt stream. Furthermore, conditions are well chosen and close to an optimal operating point at which a flow equilibrium is achieved between diheptyl ether formation and recirculation (i.e. an almost perfect flow equilibrium is achieved at a recirculation rate of approximately 40 %; i.e. a volume partition of 40 % of the bottoms relative to the total dosage). However, 360.3 g (20.000 mol) of water were formed corresponding to a yield of 70.5 %.

[0211] These conditions are suitable for mass production.

Claims

1. Process for the preparation of alkanediols having 5 to 15 carbon atoms comprising the following steps:
 - a) providing a 1-alcohol having 5 to 15 carbon atoms and/or a dialkylether having 10 to 30 carbon atoms and a catalyst;
 - b) dehydrating the 1-alcohol and/or cleavage of the dialkylether to obtain at least one alkene having 5 to 15 carbon atoms, wherein the at least one alkene having 5 to 15 carbon atoms is at least one olefin selected from the group consisting of: α -, β - and/or γ -olefins;
wherein the dehydration and/or cleavage is performed with recirculation of dialkylether and 1-alcohol; and
wherein the dehydration and/or cleavage is performed at a temperature ranging from 255 °C to 290 °C;
 - c) reaction of the at least one alkene to obtain a product comprising or consisting of at least one alkanediol having 5 to 15 carbon atoms.
2. Process for the preparation of alkanediols having 5 to 15 carbon atoms according to claim 1, wherein in step c) a product is obtained comprising or consisting of at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms;
wherein in the product, the ratio of the 1,2-alkanediol to the 2,3-alkanediol is in the range of 90 : 10 to 99.9 : 0.1 and/or the ratio of the 1,2-alkanediol to the 3,4-alkanediol is in the range of 90 : 10 to 99.99 : 0.01.
3. Process according to claims 1 or 2, wherein the 1-alcohol has 6 to 9 carbon atoms.
4. Process according to any one of claims 1 to 3, wherein the catalyst is unmodified γ -alumina.
5. Process according to any one of claims 1 to 4, wherein the dehydration and/or cleavage is performed at a temperature ranging from 270 °C to 280 °C.

6. Process according to any one of claims 1 to 5, wherein the liquid hourly space velocity of the reactants over the catalyst within the reaction chamber is ranging from 0.5 to 10 1/h, preferably 1 to 5 1/h.
7. Process according to any one of claims 1 to 6, wherein the reaction chamber is a fixed bed reactor.
8. Process according to any one of claims 1 to 7, wherein dialkylether and 1-alcohol are recirculated and combined with fresh 1-alcohol and/or fresh dialkylether, preferably fresh 1-alcohol, in a ratio of 95 : 5 to 5 : 95, preferably in a ratio of 80 : 20 to 20 : 80.
9. Process according to any one of claims 1 to 8, wherein the dehydration step b) is performed as a continuous steady-state process.
10. Process according to any one of claims 1 to 9, wherein the process additionally comprises at least one distillation step after step b) and/or step c).
11. Process according to any one of claim 1 to 10, wherein step c) is accomplished by reacting the at least one alkene with formic acid and peroxide followed by subsequent reaction with water and sodium hydroxide.
12. Composition comprising at least two alkanediols selected from the group consisting of: 1,2-alkanediols, 2,3-alkanediols and 3,4-alkanediols, each independently having 5 to 15 carbon atoms;
wherein the ratio of the 1,2-alkanol to the 2,3-alkanol is in the range of 90 : 10 to 99.9 : 0.1 and/or
wherein the ratio of the 1,2-alkanol to the 3,4-alkanol is in the range of 90 : 10 to 99.99 : 0.01.
13. Use of the composition according to claim 12 for the preparation of consumer products such as cosmetics, personal care products, in particular skin cleaning products, shampoos, rinse-off conditioners, deodorants, antiperspirants, body

lotions, textile care products, household products, in particular liquid detergents, all-purpose cleaners, laundry and cleaning agents, fabric softeners, scent boosters, fragrance enhancers and pharmaceutical compositions.

14. Consumer products such as cosmetics, personal care products, in particular skin cleaning products, shampoos, rinse-off conditioners, deodorants, antiperspirants, body lotions, textile care products, household products, in particular liquid detergents, all-purpose cleaners, laundry and cleaning agents, fabric softeners, scent boosters, fragrance enhancers and pharmaceutical compositions comprising the composition according to claim 13.

Figures

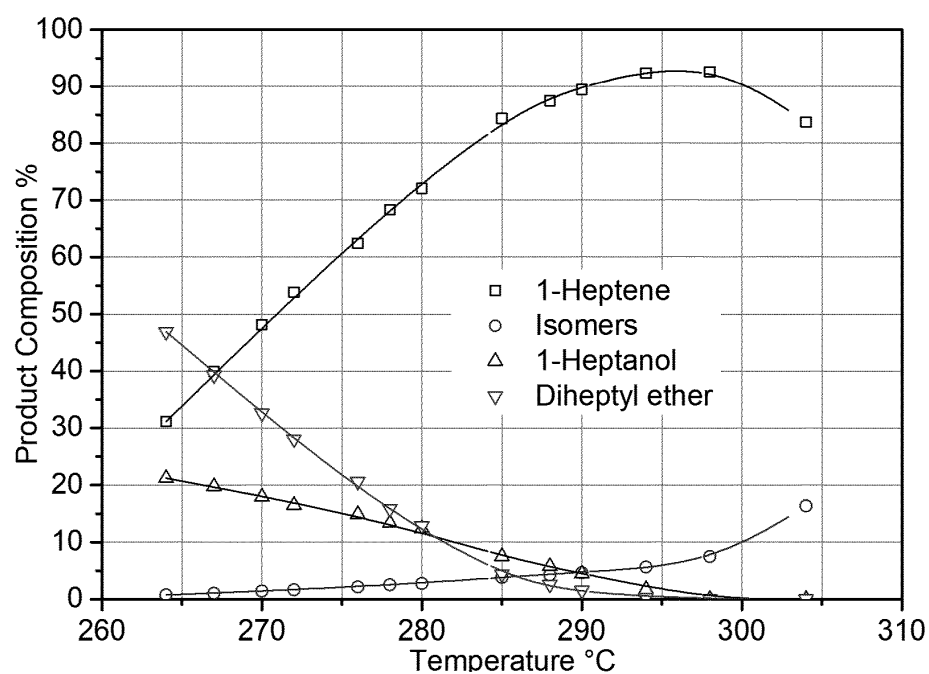


Figure 1A

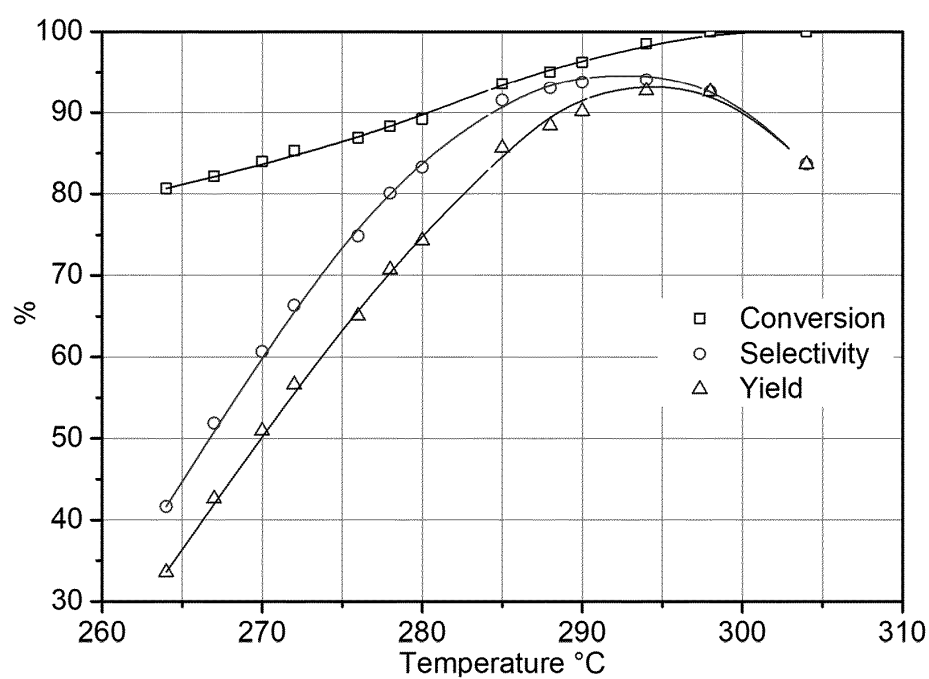


Figure 1B

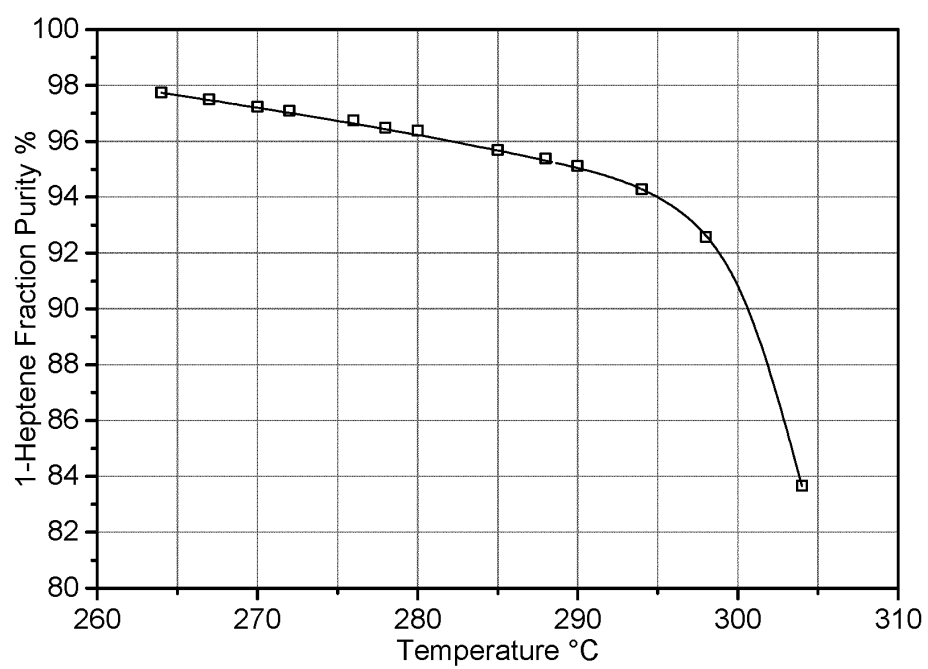


Figure 1C

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/085177

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C1/20 C07C1/24 C07C11/02
 ADD.

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)

C07C

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/152569 A2 (INOLEX INVESTMENT CORP [US]) 8 August 2019 (2019-08-08) cited in the application	12-14
A	claims 42-55	1-11
X	WO 2019/029808 A1 (SYMRISE AG [DE]) 14 February 2019 (2019-02-14) claims 13,14; tables 8,10,11,43,45	12-14
X	WO 2006/069953 A1 (SYMRISE GMBH & CO KG [DE]; SCHMAUS GERHARD [DE]; PILLAI RAVIKUMAR [US]) 6 July 2006 (2006-07-06) Claims, examples	12-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of the actual completion of the international search

4 February 2021

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/085177

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