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January 17, 2024

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VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	Francesco Baratto, et al.	)
Serial No.:	TBD	) Art Unit) TBD
Filed:	Concurrently Herewith	)
Confirmation No.:	TBD	)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
Examiner:	TBD	)
Customer No.:	116407	)

PRELIMINARY AMENDMENT

VIA *e*FILE AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Amendments to the Specification begin on page 2 of this paper.

Amendments to the Claims are reflected in the listing of claims which begins on page 3 of this paper.

Remarks/Arguments begin on page 7 of this paper.

AMENDMENTS TO THE SPECIFICATION

Please replace the abstract with the following amended abstract:

Process for the synthesis of ammonia from natural gas comprising conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or oxygen, into a synthesis gas~~ (11)~~, and treatment of the synthesis gas~~ (11)~~ with shift reaction and decarbonation, wherein a part of the CO2-depleted synthesis gas, obtained after decarbonation, is separated and used as fuel fraction for one or more furnaces of the conversion section, and the remaining part of the gas is used to produce ammonia.

AMENDMENTS TO THE CLAIMS

The listing of claims will replace all prior versions and listings of claims in the application:

Listing of Claims:

1-18. (Canceled)

19. (New) A process for synthesis of ammonia from natural gas, the process comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO2, in a conversion section;

treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

separation of a part of said CO2-depleted synthesis gas as fuel fraction, wherein said fuel fraction is fed as fuel to at least one furnace and wherein said separation of the fuel fraction includes the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.

20. (New) The process of claim 19, wherein the first stream forms the fuel fraction and the second stream is the process gas intended for the synthesis of ammonia after further purification.

21. (New) The process of claim 19, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.

22. (New) The process of claim 19, wherein said fuel fraction is between 10% and 30% of the total amount of said CO2-depleted syngas.

23. (New) The process of claim 19, further comprising a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas.

24. (New) The process of claim 23, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

25. (New) The process of claim 19, wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.

26. (New) The process of claim 19, wherein said enriched air contains at least 50% oxygen.

27. (New) The process of claim 19, wherein said enriched air contains at least 90% oxygen.

28. (New) The process of claim 19, wherein said fuel fraction of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; or one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

29. (New) The process of claim 19, wherein: a purge gas of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in the purge gas, obtaining a hydrogen-rich gas and a tail gas containing methane; at least part of said tail gas is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

30. (New) The process of claim 19, wherein: a part of said CO2-depleted syngas is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

31. (New) The process of claim 19, further comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas, after heating the CO2-depleted syngas.

32. (New) The process of claim 19, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0.

33. (New) The process of claim 19, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.

34. (New) The process of claim 19, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.

35. (New) The process of claim 19, wherein

said synthesis gas fuel fraction forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

36. (New) The process of claim 19, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process; and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

37. (New) The process of claim 19, wherein:

the conversion of the natural gas charge into synthesis gas includes a step of autothermal reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

38. (New) The process of claim 19, wherein the conversion of the natural gas into synthesis gas includes primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

39. (New) A method for revamping a plant for synthesis of ammonia from natural gas or ammonia/urea plant, wherein the plant includes a reforming section that includes a primary steam reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation; the method comprising:

providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

40. (New) The method of claim 39, further comprising installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

41. (New) The method of claim 39, wherein the section for treatment of the synthesis gas by the shift reaction of carbon monoxide includes methanation.

REMARKS

By this Preliminary Amendment, claims 1-18 are canceled; claims 19-41 are added; and the abstract is amended to remove reference numerals. Claims 19-41 are now pending in view of the above amendments. Entry of the amendments herein is respectfully requested prior to examination of the application and favorable consideration of the pending claims.

The claim amendments presented herein are for one or more of removing claim multiple dependencies, removing reference numerals, improving claim formatting, or correcting typographical errors. The claim amendments presented herein are not for reasons related to patentability.

In the event that the Examiner finds any remaining impediment to allowance of this application that may be clarified through a telephone interview, the Examiner is requested to contact the undersigned attorney. With respect to the above-identified application, the Commissioner is authorized to charge any fees under 37 C.F.R. §§ 1.16 and 1.17 which may be required and to treat any concurrent or future reply requiring a petition for an extension of time under 37 C.F.R. § 1.136(a)(3) for its timely submission as incorporating a petition therefor for the appropriate length of time and to charge any fees which may be required during the course of prosecution, or credit any overpayment, to Deposit Account No. 50-6181.

Dated this 13th day of August, 2019

Respectfully submitted,

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MSS:hm
PRELIMINARY AMENDMENT.DOC

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	TBD
	Filing Date	August 13, 2019
	First Named Inventor	Francesco Baratto
	Art Unit	TBD
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	Attorney Docket Number	283386WOUS01_495230-44

U.S.PATENT APPLICATION PUBLICATIONS

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		20040234426	A1	2004-11-25	Reddy et al.	
		20140248205	A1	2014-09-04	Allam	
		20150031916	A1	2015-01-29	Kiss	

FOREIGN PATENT DOCUMENTS

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T[5]
		2010018550	WO	A1	2010-02-18	Vakil et al.		

NON-PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
		International Preliminary Report on Patentability for International Application No. PCT/EP2018/052358 completed May 10, 2019	
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	Examiner Name	TBD
	Attorney Docket Number	283386WOUS01_495230-44

EXAMINER SIGNATURE			
Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document.
[4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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	Art Unit	TBD
	Examiner Name	TBD
	Attorney Docket Number	283386WOUS01_495230-44

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e) (1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e) (2).

☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Marcus S. Simon, Reg.# 50258/	Date (YYYY-MM-DD)	2019-08-13
Name/Print	Marcus S Simon	Registration Number	50258

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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(54) Title: NOVEL STEAM REFORMER BASED HYDROGEN PLANT SCHEME FOR ENHANCED CARBON DIOXIDE RECOVERY

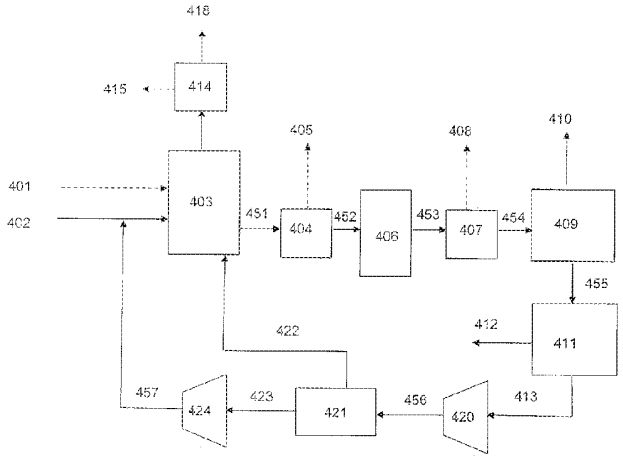


Figure 4

(57) Abstract: A novel steam reformer unit design, a novel hydrogen PSA unit design, a novel hydrogen/nitrogen enrichment unit design, and novel processing scheme application are presented. The result of these innovations results in re-allocating most of the total hydrogen plant CO2 emissions load to high pressure syngas stream exiting the water gas shift reactor while minimizing the CO2 emissions load from the reformer furnace flue gas. As compared to the conventional 60/40 split of total CO2 emissions in syngas/flue gas streams for steam reformer based conventional hydrogen plant designs, the present invention results in 85/15 or better CO2 split. This will permit about 85% or better of the total CO2 emissions load to be captured from the syngas stream, using the conventional, well proven and cost effective amine scrubbing technology. Such 85% or better CO2 capture is much greater than the 55% to 60% maximum possible using conventional steam reformer based hydrogen plant technology. As CO2 recovery from high pressure syngas stream is much easier and cost effective as compared to that from low pressure reformer furnace flue gases, a major cost benefit for equivalent CO2 recovery results with the present invention.

WO 2010/018550 A1

NOVEL STEAM REFORMER BASED HYDROGEN PLANT SCHEME FOR ENHANCED CARBON DIOXIDE RECOVERY

Field of the Invention

This invention relates to novel steam reformer unit design, a novel hydrogen PSA unit design, a novel hydrogen/nitrogen enrichment unit design, and a novel processing scheme application.

Background

The production of hydrogen by the steam reforming of hydrocarbons is well known. In the basic process, a hydrocarbon, or a mixture of hydrocarbons, is initially treated to remove, or convert and then remove, trace contaminants, such as sulfur and olefins, which would adversely affect the reformer and the down stream water gas shift unit catalyst. Natural gas containing predominantly methane is a preferred starting material since it has a higher proportion of hydrogen than other hydrocarbons. However, light hydrocarbons or refinery off gases containing hydrocarbons, or refinery streams such as LPG, naphtha hydrocarbons or others readily available light feeds might be utilized as well.

The pretreated hydrocarbon feed stream is typically at a pressure of about 200 to 400 psig, and combined with high pressure steam, which is at a higher than the feed stream pressure, before entering the reformer furnace. The amount of steam added is much in excess of the stoichiometric amount. The reformer itself conventionally contains tubes packed with catalyst through which the steam/hydrocarbon mixture passes. An elevated temperature, e.g. about 1580° F, or 860° C, is maintained to drive the endothermic reaction.

The effluent from the reformer furnace is principally hydrogen, carbon monoxide, carbon dioxide, water vapor, and methane in proportion close to equilibrium amounts at the furnace temperature and pressure. The effluent

is conventionally introduced into a one- or two-stage water gas shift reactor to form additional hydrogen and carbon dioxide. The shift reactor converts the carbon monoxide to carbon dioxide by reaction with water vapor, which generates additional Hydrogen. This reaction is endothermic. The combination of steam reformer and water gas shift converter is well known to those of ordinary skill in the art.

If CO2 capture from the high pressure syngas stream exiting the water gas shift unit is desired, the shift converter effluent, which comprises hydrogen, carbon dioxide and water with minor quantities of methane and carbon monoxide is introduced into a conventional absorption unit for carbon dioxide removal. Such a unit operates on the well-known amine wash or Benfield processes wherein carbon dioxide is removed from the effluent by dissolution in an absorbent solution, i.e. an amine solution or potassium carbonate solution, respectively. Conventionally, such units can remove up to 99 percent or higher of the carbon dioxide in the shift converter effluent.

The effluent from the carbon dioxide absorption unit is introduced into a pressure swing adsorption (PSA) unit. PSA is a well-known process for separating essentially pure hydrogen from the mixture of gases as a result of the difference in the degree of adsorption among them on a particulate adsorbent retained in a stationary bed.

Conventionally, the remainder of the PSA unit feed components, after recovery of pure hydrogen product, which comprises carbon monoxide, the hydrocarbon, i.e. methane, hydrogen and carbon dioxide, is returned to the steam reformer furnace and combusted to obtain energy for use therein

To practice CO2 emissions capture from such hydrogen plants, one must consider total emissions resulting from the plant, which includes CO2 recovery from reformer furnace flue gas as well.

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The CO2 emissions from a steam reformer based conventional hydrogen plant originate from the reformer furnace flue gas. The root source of this total CO2 in the furnace flue gas results from two sources:

(a) the reaction within the reformer tubes and shift; and

(b) the combustion of fuel in reformer furnace.

(c)

Each source contributes between about 40 and about 60% of the total CO2 emitted through the reformer furnace flue gas. For CO2 capture, conventional schemes employed consist of:

(a) removal of CO2, only from the high pressure syngas stream exit shift unit;

(b) removal of CO2, only from the reformer furnace flue gas; and

(c) removal of CO2 via both (a) and (b) above.

(d)

Option (a) permits about 50 to about 60% of total CO2 emissions capture. Option (b) permits about 90% of total CO2 emissions capture. Option (c) permits about 95% of the total CO2 emissions capture. Option (a) permits only partial capture at reasonable cost, Option (b) is considered the most expensive of the three options, capital and utility requirements wise. Option (c) is also expensive, utility intensive and quite elaborate.

Therefore, it is very desirable and cost effective to have a H2 plant design that results in between about 85% and about 95%+ of total CO2 capture, solely from the high pressure syngas stream exit water gas shift reactor.

Summary

The present invention is a novel steam reformer design and method using the same. This method includes a variety of steps of which the first is to provide a first gas mixture This first gas mixture may comprise natural gas containing mostly methane, light hydrocarbons, refinery off gases containing hydrocarbons, refinery streams such as LPG, naphtha

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hydrocarbons or other readily available light feeds. Step two involves introducing said first gas mixture into either a pre-reformer followed by a primary reformer, or directly into a primary reformer, thereby generating a second gas mixture comprising hydrogen, carbon monoxide, carbon dioxide. The novelty here is in the design and operating parameters of the primary reformer. The third step of the method includes introducing said second gas mixture into at least one isothermal shift reactor, or a combination of a high followed by a low temperature shift reactor, or a medium temperature shift reactor, thereby generating a third gas mixture. Step four includes introducing said third gas mixture into an amine wash, wherein said third gas is separated into a fourth gas mixture and a carbon dioxide enriched stream. The fifth step includes introducing said fourth gas mixture into a standard hydrogen PSA, wherein said fourth gas is separated into a hydrogen enriched stream and a PSA purge gas stream. In the final step, the reformer furnace uses the PSA purge gas as fuel with the supplemental fuel or remainder of the fuel for the reformer furnace being natural gas or a portion of the feed hydrocarbon stream, or any other external fuel . By virtue of the novel reformer, the syngas/flue gas CO2 distribution is higher than the conventional design.

In one embodiment of the present invention, the novel steam reformer design along with a novel hydrogen PSA design that is lower cost is used. Additionally, this embodiment is self-sufficient in reformer furnace fuel requirements and therefore does not require any import of supplemental fuel.

This embodiment is the same with regard to steps one to four above but differs in the remaining steps. More specifically, the fifth step of this embodiment includes introducing said fourth gas mixture into either a standard recovery or a special low recovery PSA, wherein said fourth gas is separated into a hydrogen enriched stream and a PSA purge gas stream. In this particular embodiment, the reformer furnace uses all of the

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PSA purge gas as fuel. Additionally, it uses a novel hydrogen PSA design that is lower cost. By virtue of this novel PSA design, the PSA purge gas is sufficient to satisfy all fuel requirements of the reformer furnace. Because the scheme is self-sufficient in reformer furnace fuel requirements , there is no requirement of any import of supplemental fuel. By virtue of the novel reformer and the novel PSA designs, the syngas/flue gas CO2 distribution is higher than the conventional design.

In a still further embodiment of the present invention, the novel steam reformer design is used along with a novel hydrogen PSA design that is lower cost. This embodiment is self-sufficient in reformer furnace fuel requirements and therefore, does not require any import of supplemental fuel. Additionally, a second novel gas separation unit is designed to be included in this embodiment (preferably an adsorption based unit although a membrane or a cryogenic separation unit may be used) that separates the compressed primary PSA unit purge gas into two streams--one that is recycled back as feed to the reforming section and the other that is used as reformer furnace fuel. Steps one to four of this embodiment are the same with regard to steps one to four above. The fifth step includes introducing said fourth gas mixture into either a standard recovery or a special low recovery PSA, wherein said fourth gas is separated into a hydrogen enriched stream and a PSA purge gas stream. A second novel gas separation unit is additionally employed, preferably an adsorption based unit, that separates the compressed primary PSA unit purge gas into two streams, one that is recycled back as feed to the reforming section and the other that is used as reformer furnace fuel. While an adsorption based unit is preferred, a membrane or a cryogenic separation unit may also be used. The scheme is self-sufficient in reformer furnace fuel requirements and therefore, does not require any import of supplemental fuel. By virtue of the novel reformer, the novel primary hydrogen PSA, and the novel second adsorption based separation unit, the syngas/flue gas CO2 distribution is higher than the conventional design.

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Brief Description of Drawings

The invention may be understood by reference to the following description taken in conjunction with the accompanying drawings, and in which:

Figure 1 is a schematic representation of a conventional SMR based hydrogen plant with carbon dioxide recovery.

Figure 2 is a schematic representation of one embodiment of the present invention.

Figure 3 is a schematic representation of another embodiment of the present invention.

Figure 4 is a schematic representation of a still further embodiment of the present invention.

Description of Preferred Embodiments

The present invention is based on the design of a novel steam reformer unit, a novel hydrogen PSA unit design, a novel hydrogen/nitrogen enrichment unit design, and novel processing scheme application. These innovations result in re-allocating most of the total hydrogen plant CO2 emissions load to the high pressure syngas stream, or streams, exiting the water gas shift reactor while minimizing the CO2 emissions load from the reformer furnace flue gas. As compared to the conventional 60/40 split of total CO2 emissions in syngas/flue gas streams for steam reformer based conventional hydrogen plant designs, the present invention results in 85/15 or better CO2 split. This will permit about 85% or better of the total CO2 emissions load to be captured from syngas stream, using the conventional, well proven and cost effective amine scrubbing technology. Such 85% or better CO2 capture is much greater than the 55% to 60% maximum possible using conventional steam reformer based hydrogen plant technology. Since CO2 recovery from high pressure syngas stream is much easier and cost effective compared to that from low pressure

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reformer furnace flue gases, a major cost benefit for equivalent CO2 recovery results with the present invention.

The described H2 plant design would permit recovery of between about 85% and about 95% + of the total plant CO2 generation from the high pressure syngas stream as opposed to the customary 50% to 60%. Current thinking among industry experts indicates that such 85% to 95% + of total CO2 recovery is a good practical target leading to achieving goals of "greenhouse gas sequestration". In such case, it would be of significant value to have means of doing so in a cost effective way. Current conventional H2 plants use steam reformer based technology that permits only 50% to 60% of the total CO2 emissions to be recovered cost effectively from the high pressure syngas stream upstream of the PSA unit. The remaining 40% or so ends up in the reformer furnace flue gas which is at near atmospheric pressure, having low CO2 concentrations.

CO2 recovery from reformer furnace flue gas is not practiced conventionally. There are processes currently being developed due to interest in total CO2 capture . Only one or two processes can claim success in CO2 recovery from flue gases on a commercial scale though. Large scale applications using these limited processes have not yet been commercially established with long term reliable operation. The prevailing much lower CO2 partial pressure in the flue gas, resulting from low CO2 concentration and very low total flue gas pressure, makes it much more difficult to capture CO2. Further, flue gas pressure is very low, near atmospheric, which will require compression, Large flue gas volumes make this expensive. Further, presence of residual 1 mol% to 3 mol% O2 in flue gas make the application prone to severe equipment corrosion and solvent degradation due to oxidation reactions. In addition, due to the presence of contaminants such as NOX, SOX, particulates etc., the flue gas requires significant scrubbing and clean-up before it can be processed in the CO2 recovery unit. All of these factors make flue gas equipment

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very expensive and the process very energy intensive, compared to CO2 recovery for high pressure syngas stream such as the water gas shift reactor effluent.

In comparison, the CO2 recovery from high pressure, higher CO2 concentration syngas stream exit the water gas shift unit is much easier, conventional and quite a bit less expensive. The high pressure of the syngas stream, coupled with higher CO2 concentration results in a much higher CO2 partial pressure which makes CO2 removal easy. No special scrubbing or removal of contaminents is required, and the stream can be used directly in the conventional amine scrubbing unit for CO2 recovery. Such CO2 removal from high pressure syngas streams has been conventionally practiced in industry for more than 20 to 30 years.

Therefore, a process that changes the CO2 split in syngas/flue gas from conventional 60%/40% to about 95%/5% is very desirable from CO2 recovery view point.

The present invention has several novel components; these can be applied either separately, or in combination, as deemed suitable for given application at hand. The present invention is a method of re-distributing CO2 balance from reformer furnace flue gas to the high pressure syngas exit water gas shift reaction unit, and then applying concepts of gas separation using novel processes.

The conventional SMR based hydrogen plant with carbon dioxide recovery is illustrated in Figure 1. It uses a standard steam methane reformer (SMR) technology **103** followed by high temperature water gas shift reactor **106** to take a hydrocarbon stream **102** and a steam stream **101**, and to produce a hydrogen rich syngas stream containing hydrogen, a significant amount of carbon dioxide, carbon monoxide, methane, nitrogen and other

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minor impurities. This syngas is cooled in waste heat recovery equipment **104** to generate steam **105**. The syngas is then routed to a water gas shift unit **106**, typically a high temperature shift unit, for conversion of carbon monoxide to additional hydrogen by reaction with water vapor. This syngas is further cooled in waste heat recovery equipment **107** to generate steam **108**. The cooled syngas is purified in a carbon dioxide recovery unit **109**, thereby recovering carbon dioxide **110**. The 'sweet' syngas is then further purified in a pressure swing adsorber (PSA) unit **111** for recovering a relatively pure hydrogen product **112**. The residual contents of the syngas stream, after hydrogen product recovery **113** is used as fuel for the reforming furnace. Typically, the PSA purge gas is not enough to satisfy the total reformer furnace fuel requirements. The supplemental fuel requirements for the reformer furnace are provided by import NG or other suitable fuel **119**. The reformer furnace flue gas is cooled in waste heat recovery units **114** to generate steam **115** and to preheat reformer feed streams. The flue gas also contains significant amounts of carbon dioxide. Where required or desired, this carbon dioxide is removed in a special amine wash system **116**, which produces relatively pure carbon dioxide **117** and residual flue gas **118**.

Customary practice has been to not capture any CO2 from reformer furnace flue gases. In case it is desired to do so, the available current technology for carbon dioxide recovery from flue gas, is based on specially designed amine based scrubbing system. Such CO2 removal systems for low pressure flue gas stream is quite different that commonly employed for CO2 removal from high pressure syngas streams. The much lower carbon dioxide percentage in flue gas, and very low total pressure of flue gas make it very difficult to capture carbon dioxide. Flue gas CO2 revovey systems are relatively new, and tend to be expensive due to the flue gas stream containing significant amounts of water and between about 1 and about 3 mole % oxygen. The oxygen presence in flue gas tends to corrode the equipment and degrade the solvent. The low flue gas pressure and low

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carbon dioxide concentration results in very low CO2 partial pressure, which requires physically larger equipment, and the capture requires a very reactive solvent. The presence of moisture and carbon dioxide typically pose corrosion issues as well. The utility and energy requirements are significantly greater as compared to that for conventional, CO2 recovery systems from high pressure syngas stream.

In comparison, the carbon dioxide recovery from the high pressure syngas stream is much easier, without severe corrosion issues, and is much less expensive. Utility and energy requirements are significantly lower as compared to the flue gas CO2 recovery systems.

Therefore, it is very desirable and cost effective to have a hydrogen plant design that allows 85% to 95% + carbon dioxide recovery from syngas stream alone,.

The present invention would permit recovery of between about 85% and about 95% of the total plant carbon dioxide generation from a high pressure syngas stream, as opposed to the customary 50% to 60%. With this in mind, it is desirable to design an SMR (primary reformer) based process that contains between about 85% and about 95% (as opposed to the conventional art 50 to 60%) of total carbon dioxide in the high pressure syngas stream. The novel scheme will permit reasonable CO2 recovery (85% to 95%) from syngas stream alone, thereby not requiring any further CO2 recovery from flue gas. The instant invention describes process configurations, and operating conditions, which allow one to achieve these objectives:

Turning now to Figure 2 which illustrates one embodiment of the present invention, hydrocarbon stream **202** and steam stream **201** are introduced to pre-reformer followed by a novel primary reformer, or simply a novel primary reformer **203**, wherein a syngas stream **251** comprising at least carbon dioxide and hydrogen is produced. The reformer furnace flue gas is cooled in waste heat recovery units **214** to generate steam **215**, to preheat

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reformer feed streams, and residual flue gas **218** .Syngas stream **251** is sent to a waste heat recovery unit **204** to recover steam 205. The exit of waste heat recovery, stream **252** is then introduced to a high temperature shift reactor followed by a low temperature shift reactor, or alternatively either an isothermal or a medium temperature shift reactor (symbolically represented by **206**). This produces a carbon dioxide richer stream **253**. Carbon dioxide richer stream **253** is further cooled in waste heat recovery unit **207** to generate steam **208**, and a cooler syngas stream **254**. Stream **254** is introduced into a CO2 recovery unit **209** to recover enriched CO2 stream **210** and sweet syngas stream **255**. The sweet syngas stream goes to a conventional PSA unit **211**, wherein relatively pure hydrogen **212** is recovered, and residual stream **213** is sent to the primary reformer furnace as fuel. Additional supplemental fuel **219** is added to the reformer furnace as required.

Another aspect of the present invention includes the design of a novel PSA unit for H2 recovery from syngas. When this is used in conjunction with the novel steam reformer, a process results (shown in Figure 3).

Turning now to Figure 3 which illustrates another embodiment of the present invention, hydrocarbon stream **302** and steam stream **301** are introduced to pre-reformer followed by a novel primary reformer, or simply a novel primary reformer **303**, wherein a syngas stream **351** comprising at least carbon dioxide and hydrogen is produced. The reformer furnace flue gas is cooled in waste heat recovery units **314** to generate steam **315**, to preheat reformer feed streams, and residual flue gas **318** .Syngas stream **351** is sent to a waste heat recovery unit **304** to recover steam **305**. The exit of waster heat recovery stream **352** is then introduced to a high temperature shift reactor followed by a low temperature shift reactor, or alternatively either an isothermal or a medium temperature shift reactor (symbolically represented by **306**). This produces a carbon dioxide richer stream **353**. Carbon dioxide richer stream **353** is further cooled in waste

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heat recovery unit **307** to generate steam **308**, and a cooler syngas stream **354**. Stream **354** is introduced into a CO2 recovery unit **309** to recover enriched CO2 stream **310** and sweet syngas stream **355**. The sweet syngas stream goes to a novel PSA unit **311** that has intentionally designed low H2 recovery and is lower in cost than conventional, wherein relatively pure hydrogen **312** is recovered, and residual stream **313** is sent to the primary reformer furnace as fuel. Additional supplemental fuel is not required.

Another aspect of the invention includes the design of a novel PSA unit for H2 recovery from syngas. When this is used in conjunction with the novel steam reformer, a process results (shown in **Figure 4**).

Turning now to Figure 4 which illustrates another embodiment of the present invention, hydrocarbon stream **402** and steam stream **401** are introduced to pre-reformer followed by a novel primary reformer, or simply a novel primary reformer **403**, wherein a syngas stream **451** comprising at least carbon dioxide and hydrogen is produced. Syngas stream **451** is sent to a waste heat recovery unit **404** to recover steam **405**. The exit of waster heat recovery stream **452** is then introduced to a high temperature shift reactor followed by a low temperature shift reactor, or alternatively either an isothermal or a medium temperature shift reactor (symbolically represented by **406**). This produces a carbon dioxide richer stream **453**. Carbon dioxide richer stream **453** is further cooled in waste heat recovery unit **407** to generate steam **408**, and a cooler syngas stream **454**. Stream **454** is introduced into a CO2 recovery unit **409** to recover enriched CO2 stream **410** and sweet syngas stream **455**. The sweet syngas stream **455** goes to a novel PSA unit **411** that has been intentionally designed for low H2 recovery and is lower in cost than conventional designs, wherein relatively pure hydrogen **412** is recovered. In some variations, the PSA unit **411** can be a conventional unit with conventional H2 recovery to save costs of tail gas **413** compression. The residual tail gas stream **413** is compressed in

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unit **420** to obtain compressed tail gas stream **456** which is sent to another novel gas separation unit **421** (adsorption based preferred, but a membrane or a cryogenic unit may also be used) where the tail gas stream is separated into two streams: one enriched in nitrogen and hydrogen, and the other enriched in hydrocarbons. The hydrogen and nitrogen enriched stream will have at least 40% of the total nitrogen present in the feed to the unit, along with at least 90% of the hydrogen present in the feed to the unit. The hydrogen / nitrogen rich stream **422** is sent to the primary reformer furnace **403** as fuel and the other hydrocarbon rich stream **423** is compressed in unit **424** to form?? stream **457**. Stream **457** is recycled to the reformer area as partial feed. Additional supplemental fuel is not required.

It will be recognized that the novel steam reformer, the novel H2 PSA, and the separation of the PSA purge gas using a novel process are novel process unit designs of this invention, with specific operating conditions of, at least, temperature, pressure, and composition, and concept and/or application in some cases, which are novel; all other units by themselves are conventional.

The following examples illustrate some details and benefits of the present invention.

Note, as used herein, the term "steam to carbon ratio" is understood to have units of Lb-mole steam / Lb-atoms of carbon.

Base case (Figure 1): Conventional Hydrogen Plant Design

- Supplemental hydrocarbon fuel required
- Low temperature shift not used
- Standard reformer process and furnace conditions (size = 100% base)
- Standard PSA design and recovery

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- Standard steam to carbon ratio
- 100 to 120 MMSCFD hydrogen product flow
- About 57% of total carbon dioxide recovered from syngas
- Carbon dioxide released to the atmosphere from flue gas (43% of total)
- No flue gas CO2 recovery practiced.
- Plant efficiency at 100% base.

EXAMPLE 1: (Figure 2)

- Supplemental hydrocarbon fuel not required
- Low temperature shift used
- Novel reformer process and furnace conditions (size = same as base)
- Standard PSA design and recovery
- Novel steam to carbon ratio
- Hydrogen product flow (100% of base)
- Carbon dioxide recovered from syngas (67% of total)
- Carbon dioxide released to the atmosphere from flue gas (33% of total)
- No flue gas carbon dioxide recovery employed
- Plant efficiency (marginally better than base)

EXAMPLE 2 (Figure 3):

- Supplemental hydrocarbon fuel not required
- Low temperature shift used
- Novel reformer process and furnace conditions (size = 100% base)
- Novel PSA design and recovery (less beds used, less expensive than base)
- Novel steam to carbon ratio
- Hydrogen product flow (70% of base)
- Carbon dioxide recovered from syngas (89% of total)

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- Carbon dioxide released to the atmosphere from flue gas (11% of total)
- No flue gas carbon dioxide recovery required
- Plant energy within 8% of base.

EXAMPLE 3 (Figure 3):

- Supplemental hydrocarbon fuel not required
- Low temperature shift used
- Novel reformer process and furnace conditions (size = 133% base)
- Novel PSA design and recovery (less beds used, less expensive than base)
- Novel steam to carbon ratio
- Hydrogen product flow (100% of base)
- Carbon dioxide recovered from syngas (90% of total)
- Carbon dioxide released to the atmosphere from flue gas (10% of total)
- No flue gas carbon dioxide recovery required
- Plant energy within 7% of base.

EXAMPLE 4 (Figure 4):

- Supplemental hydrocarbon fuel not required
- Low temperature shift used
- Novel reformer process and furnace conditions (size = 100% base)
- Novel PSA design and recovery (less beds used, less expensive than base)
- Novel steam to carbon ratio
- Hydrogen product flow (69% of base)
- Carbon dioxide recovered from syngas (> 98% of total)
- Carbon dioxide released to the atmosphere from flue gas (< 2% of total)
- Novel tail gas separation unit employed for recycle to reformer feed

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- No flue gas carbon dioxide recovery required
- Plant energy within 12% of base.

EXAMPLE 5 (Figure 4):

- Supplemental hydrocarbon fuel not required
- Low temperature shift used
- Novel reformer process and furnace conditions (size = 133% base)
- Novel PSA design and recovery (less beds used, less expensive than base)
- Novel steam to carbon ratio
- Hydrogen product flow (100% of base)
- Carbon dioxide recovered from syngas (> 98% of total)
- Carbon dioxide released to the atmosphere from flue gas (< 2% of total)
- Novel tail gas separation unit employed for recycle to reformer feed
- No flue gas carbon dioxide recovery required
- Plant energy within 9% of base.

In another embodiment of the present invention the primary reformer tube exit temperatures is between about 1700° F (927° C) and about 1750° F (954° C), preferably about 1730° F (943° C). This is in contrast with the conventional primary reformer tube exit temperature of between about 1600° F (871° C) and about 1650° F (899° C).

In another embodiment of the present invention, the primary reformer furnace bridge wall temperatures is between about 1850° F (1010° C) and 1950° F (1066° C), preferably about 1900° F (1038° C). This is in contrast with the conventional primary reformer furnace bridge wall temperatures of between about 1950° F (1066° C) and about 2050° F (1121° C). The temperature difference at the reformer furnace bridge wall, is herein

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defined as the bridge wall temperature minus the primary reformer tube exit temperature.

In a still further embodiment, a carbon ratio of between about 3.0 and 4.0, preferably about 3.2, is used. This is in contrast to the conventional value of about 2.8.

In yet another embodiment, other process conditions such as pressure, temperature and composition are adjusted as necessary in order to achieve no more than about 1 mol% (preferably less than about 0.5%) dry carbon monoxide slip and about 2 mol% (preferably less than about 0.5%) dry methane slip in the syngas stream at the inlet to the PSA, both on dry mol% basis.

In another embodiment, a low recovery PSA is used to recover only an amount of hydrogen that leaves enough un-recovered PSA purge gas stream sufficient to satisfy total supplemental fuel requirements of the reformer furnace. This low recovery PSA has a hydrogen recovery of between about 50% and about 65%, in contrast with the conventional system which has a hydrogen recovery of about 87%. The use of a low recovery PSA will preclude the need for any external hydrocarbon based supplemental fuel requirement. The use of such low recovery PSA designs will permit the use of less adsorption beds, typically between 4 and 10, preferably between 5 and 9, more preferably between 6 and 8, and still more preferably between 4 and 5.. This is contrasted with the 10 to 14 beds typically required for a hydrogen plant with 100 to 120 MMSCFD (28,316 to 33,979 NCMD at 16 °C) hydrogen product capacity.

In still another embodiment, the PSA hydrogen recovery is adjusted so that the purge fuel gas from the PSA flow is sufficient for all fuel demands in the primary reformer furnace. No additional supplemental fuel is used.

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In yet still another embodiment, the primary reformer furnace excess air is adjusted in order to achieve a stable flame with essentially all of the hydrogen containing fuel, while establishing a reasonable limit on adiabatic flame temperature (typically less than about 4000° F, 2204° C).

In another embodiment, at least about 99% of the available carbon dioxide is recovered from a high pressure syngas stream upstream of PSA using a conventional technology such as, but not limited to, aMDEA, that are well proven and cost effective from capital and energy requirements view point. Any appropriate conventional technology known to the skilled artisan is appropriate.

In another embodiment, the novel PSA design permits higher than 1.2 Bara (17.4 psia) PSA purge gas pressure (typically between about 5 Bara and about 10 Bara, or about 72.5 psia and about 145 psia) due to the reduced recovery needs. The higher pressure helps minimize the size and cost of the associated compressor upstream of either an associated novel adsorption unit, a membrane unit or a cold box unit for further tail gas separation.

In another embodiment, a novel stand alone adsorption based gas separation unit is included for separation of the PSA (conventional or novel hydrogen PSA design down stream of syngas CO2 removal unit). This novel unit separates the PSA tail gas (purge gas) post compression, into two gas streams: one rich in H2 and N2, and the other rich in hydrocarbons. The H2/N2 rich stream is used as fuel in the reformer furnace; the hydrocarbon rich stream is compressed and recycled back to the reformer as feed.

In another embodiment, the membrane system may be operated at suitable pressures by further compressing the PSA purge gas (that exits the PSA unit at between about 5 Bara and about 10 Bara (about 72.5 psia and

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about 145 psia) such that the residue hydrocarbon stream exiting the membrane unit can be recycled back as part feed to the reformer without further compression. The membrane permeate stream will be used as fuel in the reformer furnace. No additional supplemental fuel will need to be imported.

In another embodiment, where the cold box / membrane system is employed on novel PSA tail gas (at 5 to 10 Bara pressure, about 72.5 psia and about 145 psia), an aMDEA unit, for syngas CO2 recovery is not required, as the cold box unit recovers carbon dioxide from the PSA purge gas (after compression) in a cold box type cryogenic carbon dioxide separation unit. The remaining stream from the cold box is processed in a membrane unit to recover two separate streams; a raw hydrogen stream at low pressure (but greater than about 1.2 Bara, 17.4 psia) to be used as reformer fuel, and a second stream containing remaining hydrocarbons. This hydrocarbon stream is compressed as required, and recycled back to the reformer as part feed. A flue gas carbon dioxide recovery system is not required.

In another embodiment, at least about 99% of the available carbon dioxide is recovered from a high pressure syngas stream upstream of PSA using a conventional technology such as, but not limited to, aMDEA or a cold box/membrane unit that are well proven and cost effective from capital and energy requirements view point. Any appropriate conventional technology known to the skilled artisan is appropriate.

Other embodiments may comprise additional units such as a syngas carbon dioxide recovery unit and/or a membrane purification unit. Other embodiments may comprise additional units such as a combined cold box and/or a membrane purification unit. These additional units may be used in any combination recognized as plausible by the skilled artisan.

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Illustrative embodiments have been described above. While the method in the present application is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings, and have been herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the method in the present application to the particular forms disclosed, but on the contrary, the method in the present application is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the method in the present application, as defined by the appended claims.

It will, of course, be appreciated that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developer's specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time-consuming, but, would nevertheless, be a routine undertaking for those of ordinary skill in the art, having the benefit of this disclosure.

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What is claimed is:

1. A method of re-distributing the CO2 balance from a reformer furnace flue gas to the high pressure syngas exit water gas shift reaction unit, comprising;

- providing a first gas mixture;
- introducing said first gas mixture either into a pre-reformer followed by a primary reformer, or directly into a primary reformer, thereby generating a second gas mixture comprising hydrogen, carbon monoxide, carbon dioxide;
- introducing said second gas mixture into at least one isothermal shift reactor, or a combination of high followed by a low temperature shift reactor, or a medium temperature shift reactor, thereby generating a third gas mixture;
- introducing said third gas mixture into an amine wash, wherein said third gas is separated into a fourth gas mixture and a carbon dioxide enriched stream;
- introducing said fourth gas mixture into a standard H2 PSA unit, wherein said fourth gas is separated into a hydrogen enriched stream and a PSA purge gas stream;
- introducing said PSA purge gas stream as fuel into the reformer furnace along with natural gas, a portion of the feed hydrocarbon stream, or any other external supplemental fuel for the reformer furnace.

2. The method of claim 1, wherein said steam reformer has a tube exit temperature between about 1700° F and about 1750° F.

3. The method of claim 2, wherein said tube exit temperature is about 1730° F.

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4. The method of claim 1, wherein said steam reformer has a furnace bridge wall temperature of between about 1850° F and about 1950° F.

5. The method of claim 4, wherein said furnace bridge wall temperature is about 1900° F.

6. The method of claim 1, wherein said steam reformer has a steam to carbon ratio of between about 3.0 and about 4.0.

7. The method of claim 6, wherein said steam to carbon ratio is about 2.8.

8. The method of claim 1, wherein the excess air to the furnace of said primary reformer is adjusted in order to achieve a stable flame while maintaining an adiabatic flame temperature of about 4000° F.

9. The method of claim 1, wherein at least about 99% of the carbon dioxide present in the fourth gas stream is removed by said amine wash system.

10. A method of re-distributing CO2 balance from reformer furnace flue gas to the high pressure syngas exit water gas shift reaction unit , comprising;

- providing a first gas mixture;
- introducing said first gas mixture into a pre-reformer followed by a primary reformer, or directly into a primary reformer, thereby generating a second gas mixture comprising hydrogen, carbon monoxide, carbon dioxide;
- introducing said second gas mixture into at least one isothermal shift reactor, or a combination of high followed by a low temperature shift reactor, or a medium temperature shift reactor, thereby generating a third gas mixture;

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- introducing said third gas mixture into an amine wash, wherein said third gas is separated into a fourth gas mixture and a carbon dioxide enriched stream;
- introducing said fourth gas mixture into special low recovery PSA, wherein said fourth gas is separated into a hydrogen enriched stream and a PSA purge gas stream;
- introducing said purge gas from novel PSA to the reformer furnace as fuel;
- wherein no additional supplemental fuel is sent to the reformer furnace.

11. The method of claim 10, wherein said novel PSA has a hydrogen recovery between about 50% and about 65%.

12. The method of claim 10, wherein said PSA has reduced number of adsorption beds compared to similar size conventional units..

13. The method of claim 12, wherein the number of adsorption beds is between 8 and 10.

14. The method of claim 10, wherein the hydrogen recovery of said PSA is adjusted such that the PSA purge gas stream heat content as fuel is sufficient to satisfy the fuel demand of the primary reformer.

15. The method of claim 10 wherein the novel PSA unit delivers a sufficient quantity of fuel by varying the hydrogen % recovery within the novel PSA unit such that no additional supplemental fuel to the reformer furnace is required.

16. The method of claim 10, wherein said purge gas stream has a pressure of between about 5 bara and about 10 bara.

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17. The method of claim 10, wherein said purge gas stream has a pressure of greater than about 1.2 bara.

18. A method of separating carbon dioxide from a gas mixture, comprising;

- providing a first gas mixture;
- introducing said first gas mixture either into a pre-reformer followed by a primary reformer, or directly into a primary reformer, thereby generating a second gas mixture comprising hydrogen, carbon monoxide, carbon dioxide
- introducing said second gas mixture into at least one isothermal shift reactor, or a combination of high followed by a low temperature shift reactor, or a medium temperature shift reactor, thereby generating a third gas mixture;
- introducing said third gas mixture into an amine wash, wherein said third gas is separated into a fourth gas mixture and a carbon dioxide enriched stream;
- introducing said fourth gas mixture into either a standard recovery or a special low recovery PSA, wherein said fourth gas is separated into a hydrogen enriched stream and a PSA purge gas stream;
- compressing said PSA purge gas stream to a suitable pressure;
- introducing said compressed purge gas stream to a novel gas separation unit selected from an adsorption based unit, a membrane separation unit or a cryogenic separation unit, that separates the compressed PSA unit purge gas into two streams, a hydrogen and nitrogen enriched stream and a stream of residual gases;
- introducing the hydrogen and nitrogen enriched stream to the reformer furnace as fuel and recycling the stream of residual gases back to the reformer as partial feed after compression as required;
- wherein no additional supplemental fuel is sent to the reformer furnace.

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19. The method of claim 18, wherein said novel gas separation unit is a novel adsorption based unit.

20. The method of claim 19, wherein the said adsorption based unit can be of 4 to 5 adsorption beds.

21. The method of claim 19, wherein said hydrogen and nitrogen enriched stream will have at least 40% of the total nitrogen present in the feed to the unit, along with at least 90% of the hydrogen present in the feed to the unit.

22. The method of claim 18, wherein said residue gas stream from the novel gas separation unit is compressed to a suitable pressure.

23. The method of claim 22, wherein said high pressure residue hydrocarbon stream is recycled as part feed to the reformer.

24. The method of claim 18, wherein said novel gas separation unit is either a cryogenic process (do you mean separation unit?) or a membrane based process (do you mean separation unit??).

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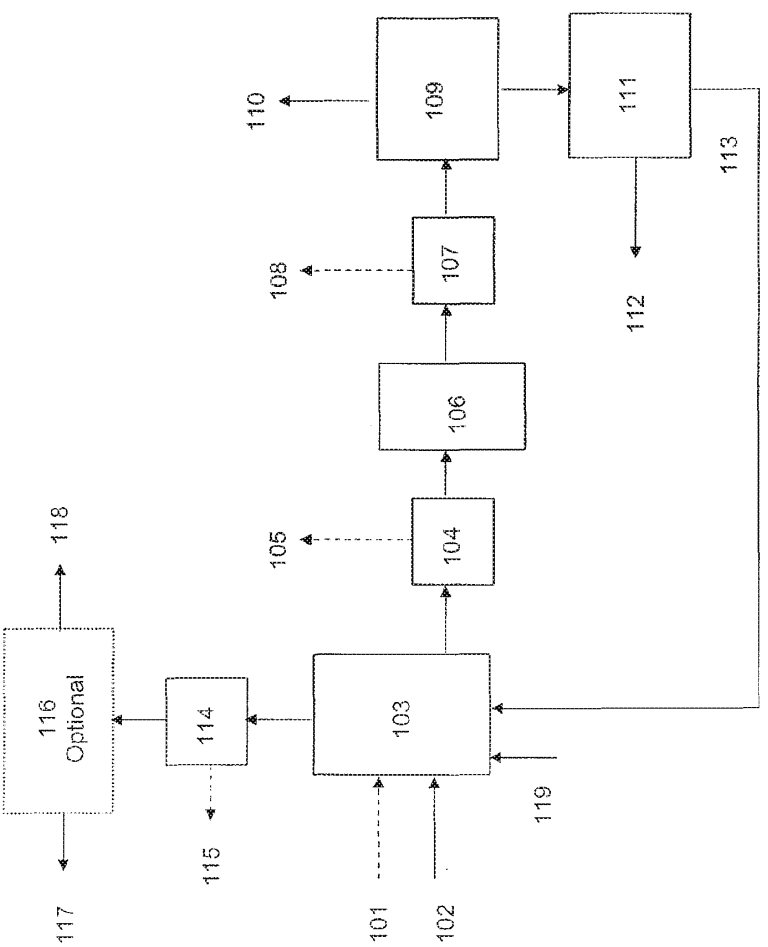

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Figure 1

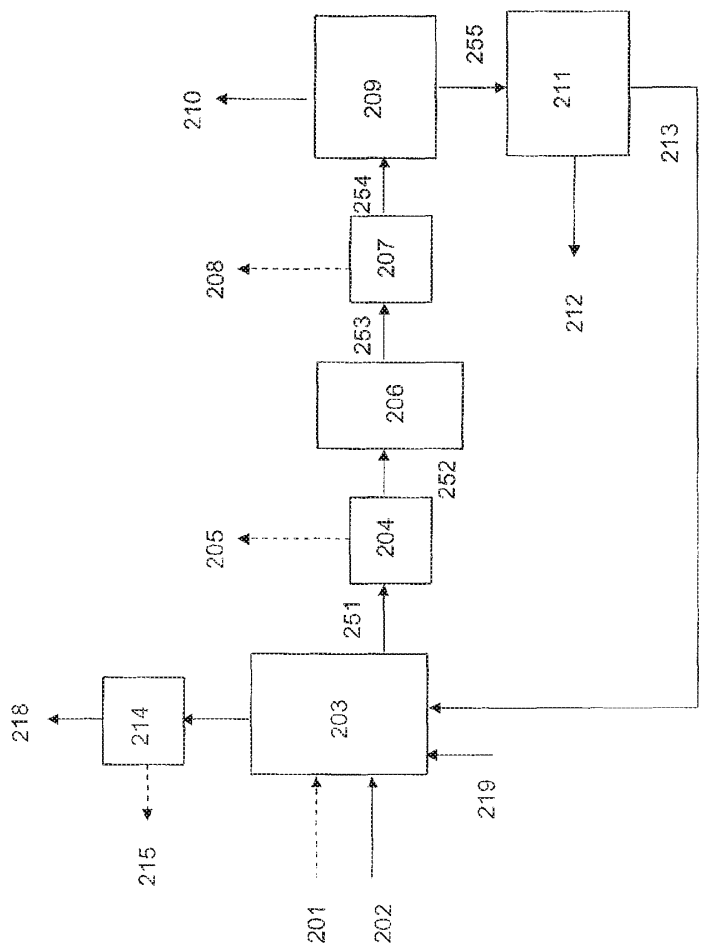

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Figure 2

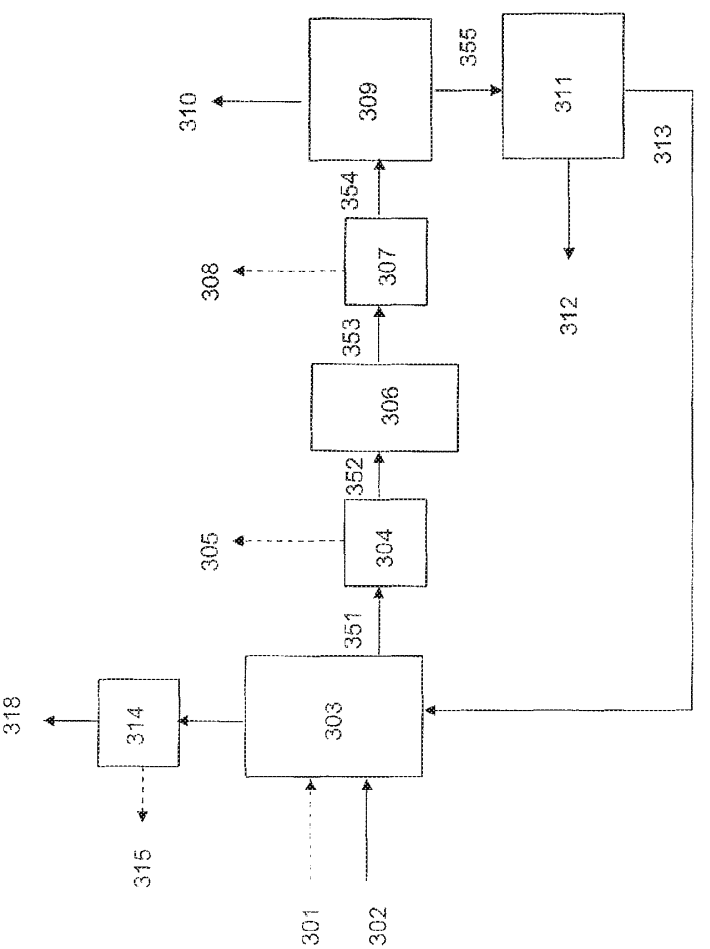

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Figure 3

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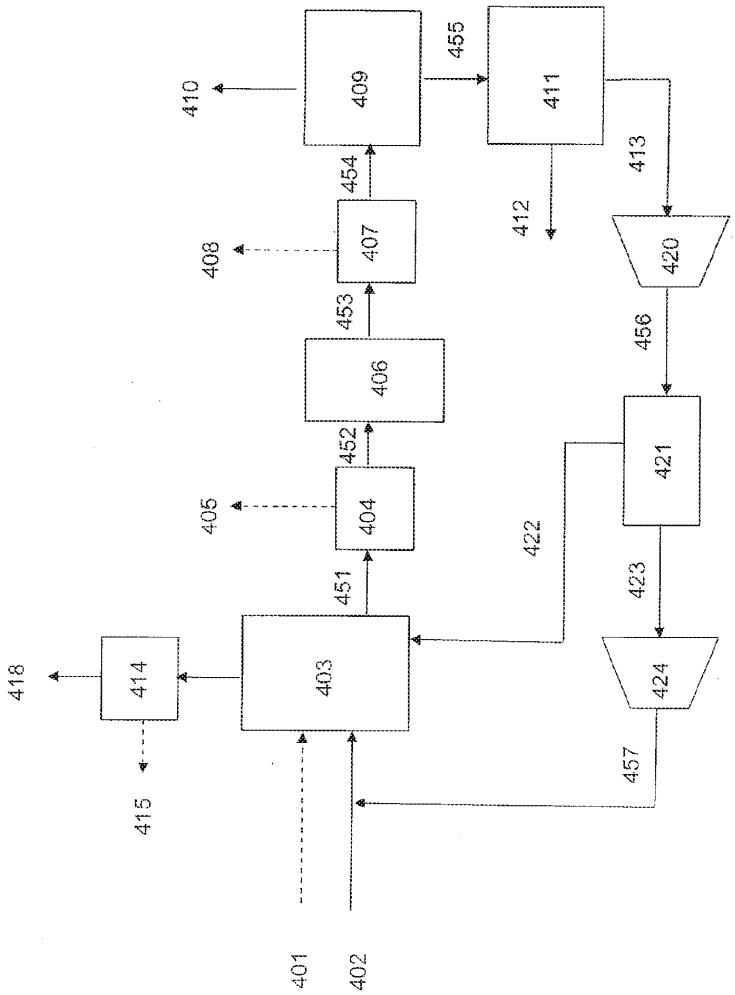


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/053566

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38 C01B3/48 C01B3/52 C01B3/56

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)
C01B

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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/171878 A1 (BLUMENFELD MICHAEL [DE] ET AL) 3 August 2006 (2006-08-03) paragraphs [0007], [0008], [0014], [0016]; figures 1,2	1-17
X	US 2002/073845 A1 (REDDY SATISH [US]) 20 June 2002 (2002-06-20) paragraphs [0014] - [0017], [0021], [0022]	18-24
A	US 4 553 981 A (FUDERER ANDRIJA [BE]) 19 November 1985 (1985-11-19) column 4, line 4 - column 6, line 68; claims 1,2,9,11; figure 1	1-24

-/--

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 November 2009	01/12/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Galleiske, Anke

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 36 02 352 A1 (LINDE AG [DE]) 30 July 1987 (1987-07-30) column 1, line 29 - column 3, line 4; figure 1	1-24
A	EP 1 146 009 A (AIR PROD & CHEM [US]) 17 October 2001 (2001-10-17) paragraph [0016]; figure 1A	1-24
A	EP 1 582 502 A (GEN ELECTRIC [US]) 5 October 2005 (2005-10-05) paragraphs [0012], [0015], [0020] - [0027], [0030]	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2009/053566

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006171878 A1	03-08-2006	AT 343545 T	15-11-2006
		CA 2534210 A1	10-02-2005
		CN 1829656 A	06-09-2006
		DE 10334590 A1	03-03-2005
		DK 1648817 T3	26-02-2007
		EP 1648817 A1	26-04-2006
		WO 2005012166 A1	10-02-2005
		ES 2275235 T3	01-06-2007
		HK 1093335 A1	13-06-2008
		JP 2007500115 T	11-01-2007
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US 2002073845 A1	20-06-2002	AT 336287 T	15-09-2006
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		MX PA03005402 A	25-09-2003
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US 4553981 A	19-11-1985	NONE	
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EP 1146009 A	17-10-2001	SG 94800 A1	18-03-2003
		US 6521143 B1	18-02-2003
EP 1582502 A	05-10-2005	CN 1676460 A	05-10-2005
		JP 2005281131 A	13-10-2005
		US 2005210881 A1	29-09-2005

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AMC121BWO	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/EP2018/052358	International filing date *(day/month/year)* 31.01.2018	Priority date *(day/month/year)* 15.02.2017
International Patent Classification (IPC) or national classification and IPC INV. C01B3/02		
Applicant Casale SA		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 7 sheets, as follows:
      - ☒ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions).
      - ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2).
      - ☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)).

   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in the form of an Annex C/ST.25 text file, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*ter* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11.06.2018	10.05.2019
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	Authorized officer Werner, Håkan Telephone No. +49 89 2399-8571

Form PCT/IPEA/ 409 (cover sheet) (January 2015)

Box No. I Basis of the report

1. With regard to the **language**, this report is based on

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3(a) and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4(a))
   - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-32 as originally filed

Claims, Numbers

1-16 filed with telefax on 14-01-2019

Drawings, Sheets

1-4 as originally filed

☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-*bis*)):
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

5. ☐ This report has been established:
   - ☐ taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-*bis*) and 70.2(e)).
   - ☐ without taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91(Rules 66.4*bis* and 70.2(e)).

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6. ☒ With regard to top-up searches (Rules 66.1*ter* and 70.2(f)):
   - ☒ A top-up search was carried out by this Authority on 23.04.2019 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
     - ☐ Additional relevant documents have been discovered during the top-up search.
   - ☐ No top-up search was carried out by this Authority because it would serve no useful purpose.

7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

* *If item 4 applies, some or all of those sheets may be marked "superseded".*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-14
	No:	Claims	15, 16
Inventive step (IS)	Yes:	Claims	1-14
	No:	Claims	15, 16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

SECTION V

1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 15 and 16 is not new in the sense of Article 33(2) PCT.

2 D1 discloses (in particular paragraphs [0023]-[0027], [0031], [0032] and [0034] and Figs. 2 and 3) a method for making ammonia comprising reforming natural gas using a gas comprising 90% oxygen from an ASU. The syngas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a coldbox whereby two streams are obtained. One stream is sent to the ammonia converter and the other stream is used as fuel in the primary reformer. Before the CO_2 depleted syngas is treated in a coldbox it is treated in a methanator. Therefore, the depleted syngas will inevitably have an amount of CO_2 < 1000ppm. The tail gas (=CO_2 depleted syngas used as fuel gas) can be compressed followed by expansion (paragraph [0031]). D1 further disclosed that existing ammonia plants can be revamped using the means disclosed in D1, namely an ASU and a coldbox with which two streams are obtained, one which is sent to the ammonia converter and the other which is used as fuel in the primary reformer.

3 Therefore, the subject-matter of claims 15 and 16 is not new vis-a-vis D1.

4 The subject-matter of claims 1-14 relates to new and inventive matter (Article 33(2) and (3) PCT).

5 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses (in particular paragraphs [0023]-[0027], [0031], [0032] and [0034] and Figs. 2 and 3) a method for making ammonia comprising reforming natural gas using a gas comprising 90% oxygen from an ASU. The syngas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a coldbox whereby two streams are obtained, a fuel stream comprising methane, H2 and N2 and a syngas stream comprising N2 and H2 in a ratio of 1:3. The syngas stream is sent to the ammonia converter and the fuel stream is used as fuel in the primary reformer.

6 The subject-matter of claim 1 therefore differs from this known process in that the two streams obtained have the same composition and is therefore new (Article 33(2) PCT).

7 The problem to be solved by the present invention may be regarded as reducing the CO2 emission from the plant.

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8 The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons: Using part of the CO2 depleted syngas as fuel in a furnace in the process reduces the CO2 emission of the process. There is no hint in the prior art this solution to the problem.

9 Claims 2-14 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

10 Further documents cited in the search report:

D2 discloses a method for making syngas. Natural gas is reformed whereby a synthesis gas is obtained. The synthesis gas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a PSA unit where a H2 rich stream and a residual stream are obtained. The residual stream comprising H2 is used as fuel in the primary reformer. With this method enhanced CO_2 recovery during steam reforming can be obtained.

D3 discloses a method for making ammonia and urea with reduced CO_2 emission. A synthesis gas is produced using oxygen from an ASU. CO in the obtained syngas is converted into CO_2. Then CO_2 is removed from the syngas with now comprises H_2. The CO_2 depleted synthesis gas is combined with N_2 from the ASU whereby ammonia is obtained. Ammonia is reacted with CO_2 whereby urea is produced. Using part of the CO_2 depleted syngas as fuel is not disclosed.

ZARDI

EUROPEAN PATENT AND TRADEMARK ATTORNEYS

EPO
EUROPEAN PATENT OFFICE
International Preliminary Examining Authority
D-80298 Munich
Germany

BY FAX (11 pages) AND MAIL

Lugano, January 14, 2019

Your file:
Our file: **AMC121BWO**

Re: International Patent Application No. **PCT/EP2018/052358**

Applicant: CASALE S.A.

Authorized Officer: W HÅKAN

Dear Sirs,

In response to the Written Opinion of the International Searching Authority pursuant to Rule 43*bis*.1 PCT dated July 31, 2018 the Applicant wishes to submit the following amendments and the following observations.

AMENDMENTS

In the claims:

Claim 1 as originally filed has been amended by inserting therein the features of dependent claim 2. Claims 2 and 16 have been deleted and the other claims renumbered accordingly.

A new set of claims 1-16 is enclosed to the present letter, which should replace the claims as originally filed, together with a copy of original claims 1-18 with hand-written amendments.

OBSERVATIONS

1. Re Item V of the Written Opinion

In the Applicant's opinion, the subject-matter of independent claim 1 should be regarded as new and inventive over the cited prior art documents D1 (US2004/0234426), D2 (WO 2010/018500), D3 (US 2015/0031916) and D4 (US 2014/0248205) for the following reasons.

In none of D1, D2 and D4 the stream fed as a fuel to the furnace is separated of a part of a CO2-depleted synthesis gas, as recited in the characterizing portion of present claim 1.

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In all these prior art documents, such a fuel stream is instead obtained through a purification step, either cryogenic or through PSA, of such a CO2 depleted synthesis gas. In other words, the fuel stream is not a stream, which is merely split from a CO2 depleted synthesis gas, as in present claim 1, but - on the contrary - it is a purge stream resulting as a by-product from the transformation process of a CO2 depleted synthesis gas into a purified synthesis gas.

Indeed, in D1, D2 and D4, the purge stream used as a fuel and the purified synthesis gas stream are not comparable the one to the other, having substantially different composition.

The subject-matter of present claim 1 thus differs from the processes of D1, D2 and D4 at least by the features recited in its characterizing portion.

Actually, the processes disclosed in these prior art documents suffer of the same drawbacks as set forth in the prior art section of the present application (see for instance page 2, lines 20-25).

As to D3, it is noted that this document cannot be regarded as relevant prior art with respect to the present invention. For sure, this document cannot be regarded as the closest prior art in connection with the claimed process.

According to the invention, a process for synthesis of ammonia from natural gas is claimed.

On the contrary in D3, gasification of waste is disclosed and taught. See for instance D3, par. [0025]. By waste reference is made to domestic waste and organic waste. See for instance D3, par. [0001], [0007]-[0009]. This has nothing to do nor can it be confused with or compared to the technical field of the present invention.

The skilled person of ammonia synthesis from natural gas would have never considered a document related to the disposal of domestic or organic waste (i.e. a document belonging to a far remote technical field) in the absence of a clear and unambiguous hint in the prior art to do so. Hint, which is however totally missing. In this regard, any assertion to the contrary should be traversed for hindsight.

In any case, even supposing – *arguendo* – to combine D3 with D1, D2 or D4, the skilled person would have still not being able to arrive in an obvious manner to the claimed process since the features recited in the characterizing section of claim 1 would have still been missing.

In summary, in view of the above-identified distinguishing features the technical problem underlying the present invention should be regarded as the one set forth in the description at page 2, line 27 to page 3, line 1. The skilled person aiming to solve such a technical problem, by considering the available prior art documents would have not been directed in an obvious manner towards the claimed process, the latter being only possible with the exercise of an inventive skill.

Any assertion stating that the subject-matter of claim 1 is obvious to the skilled person without any prior art substantiation should be traversed as being the result of an inadmissible ex-post facto analysis of the invention.

ZARDI

Therefore, the subject-matter of claim 1 should be regarded as new and also involving an inventive step in view of D1-D4 (Art. 33(2)(3) PCT).

The above observations also apply to the independent claim 15 as well as to the dependent claims 2-14 and 16.

In connection with claim 15, it is noted that the current wording of: separating a part of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion, gives no doubt about the fact that the separation takes place in the same manner as recited in claim 1 and can thus not be confused with or compared to the purification step of the prior art (see also present description, page 4, line 27 to page 5, line 3).

*** * ***

CONCLUSIONS

In consideration of the above arguments, the Applicant is of the opinion that the subject-matter of present claims 1-16 meets the requirements of patentability.

We therefore look forward to receiving a favorable International Preliminary Examination Report; however, should the Authorized Officer be of a different opinion, he is kindly requested to issue a further Written Opinion or to contact the undersigned for a telephone or personal interview according to Article 34(2)(a) and Rule 66.6 PCT.

Respectfully submitted.
The Representative
Marco Zardi
c/o M. ZARDI & Co.

Encl.: as above

CLAIMS

1) Process for synthesis of ammonia from natural gas, comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas (11) containing hydrogen, CO and CO2, in a conversion section;

a treatment of said synthesis gas (11) comprising at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas (12) and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas,

characterized by:

separation of a part (14) of said CO2-depleted synthesis gas (12) as fuel fraction, wherein said fuel fraction (14) is fed as fuel to at least one furnace and wherein said separation of the fuel fraction comprises the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia, optionally after further purification.

2) Process according to claim 1, wherein said fuel fraction (14) is comprised between 1% and 40% of the total amount of said CO2-depleted syngas (12), preferably between 10% and 30%.

3) Process according to any one of the preceding claims, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

4) Process according to any one of the preceding claims, wherein said CO2-

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depleted syngas (12) contains no more than 1000 ppm by volume of CO2.

5) Process according to any one of the preceding claims, wherein said enriched air contains at least 50% of oxygen, preferably at least 90% oxygen.

6) Process according to any one of the preceding claims, wherein said fuel fraction (14) of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

7) Process according to any one of the preceding claims, wherein: a purge gas (21) of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in it, obtaining a hydrogen-rich gas (20) and a tail gas (15) containing methane; at least part (15a) of said tail gas (15) is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

8) Process according to any one of the preceding claims, wherein: a part of said CO2-depleted syngas (12) is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, preferably all of it, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

9) Process according to any one of the preceding claims, also comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas (12), optionally after heating it.

10) Process according to any one of the preceding claims, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0, preferably greater than 2.4 and more preferably greater than 2.7.

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Duration: 01.14.2019 08:06:55 PM - 01.14.2019 08:10:04 PM. This page 5 of 11 was completed at 01.14.2019 08:08:32 PM

11) Process according to any one of the preceding claims, wherein

said synthesis gas fuel fraction (14) forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

12) Process according to any one of the preceding claims, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

13) Process according to any one of the preceding claims, wherein:

the conversion of the natural gas charge into synthesis gas comprises a step of autothermal reforming, optionally with pre-reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

14) Process according to any one of the preceding claims, wherein the conversion of the natural gas into synthesis gas comprises: primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

15) Method for revamping a plant for the synthesis of ammonia from natural gas or ammonia/urea plant, wherein

the plant comprises a reforming section which includes a primary steam

Received at the EPO on Jan 14, 2019 20:10:04. Page 6 of 11 14/01/2019
ation: 01.14.2019 08:08:55 PM - 01.14.2019 08:10:04 PM. This page 6 of 11 was completed at 01.14.2019 08:08:50 PM

reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by means of a shift reaction of carbon monoxide into carbon dioxide, decarbonation and optionally methanation.

and the revamping method comprises at least:

providing a flow (22) of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part (14) of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction (14) of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

16) Method for revamping according to claim 15 comprising: installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

Received at the EPO on Jan 14, 2019 20:10:04. Page 7 of 11 14/01/2019
ration: 01.14.2019 08:06:55 PM - 01.14.2019 08:10:04 PM. This page 7 of 11 was completed at 01.14.2019 08:09:01 PM

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3NSDOCID: <XS_____2006100103CF_1_>

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
AMC121BWO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP2018/052358	31 January 2018 (31-01-2018)	15 February 2017 (15-02-2017)
Applicant		
CASALE SA		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of:
      [X] the international application in the language in which it was filed
      [ ] a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. [ ] This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. [ ] **Certain claims were found unsearchable** (See Box No. II)

3. [ ] **Unity of invention is lacking** (see Box No III)

4. With regard to the **title**,
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,
   a. the figure of the **drawings** to be published with the abstract is Figure No. 1
      [X] as suggested by the applicant
      [ ] as selected by this Authority, because the applicant failed to suggest a figure
      [ ] as selected by this Authority, because this figure better characterizes the invention
   b. [ ] none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/052358

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/02 C01B3/36 C01C1/04
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)
C01B C01C

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, CHEM ABS Data, 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 A	US 2004/234426 A1 (REDDY SATISH [US] ET AL) 25 November 2004 (2004-11-25) paragraphs [0023] - [0027], [0031], [0032], [0034]; figures 2,3	1,3,5-8, 10,14-18 2,4,9, 11-13
Y A	WO 2010/018550 A1 (AIR LIQUIDE [FR]; VAKIL TARUN D [US]; WOLF ULRICH [DE]) 18 February 2010 (2010-02-18) page 3, line 23 - page 4, line 19; claim 7; figures 2,3 page 11, line 20 - page 12, line 8 page 17, lines 15-27	1,3-7, 11,12, 15-18 2,8-10, 13,14
Y A	US 2015/031916 A1 (KISS GUENTER HANS [CH]) 29 January 2015 (2015-01-29) paragraphs [0012] - [0020]; figure 1	1,3-7, 11,12, 14-18 2,8-10, 13
	-/--	

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 July 2018	31/07/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Werner, Håkan

3

Form PCT/ISA/210 (second sheet) (April 2005)

Topsoe, Inc. – EX1002
Page 59 of 356

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/052358

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014/248205 A1 (ALLAM RODNEY J [GB]) 4 September 2014 (2014-09-04) paragraphs [0021], [0022], [0034] - [0038]; figure 2 -----	1,7,14

3

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

Topsoe, Inc. – EX1002
Page 60 of 356

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/052358

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004234426 A1	25-11-2004	AU 2002310519 B2	31-08-2006
		CA 2449503 A1	09-01-2003
		EP 1401766 A1	31-03-2004
		JP 4358617 B2	04-11-2009
		JP 2004531451 A	14-10-2004
		MX PA03011337 A	19-03-2004
		US 2004234426 A1	25-11-2004
		WO 03002459 A1	09-01-2003
WO 2010018550 A1	18-02-2010	CA 2643778 A1	13-02-2010
		EA 201170328 A1	31-10-2011
		EP 2321217 A1	18-05-2011
		US 2010037521 A1	18-02-2010
		US 2012141368 A1	07-06-2012
		WO 2010018550 A1	18-02-2010
US 2015031916 A1	29-01-2015	NONE	
US 2014248205 A1	04-09-2014	AU 2011258160 B2	03-09-2015
		CA 2800508 A1	01-12-2011
		CN 103025649 A	03-04-2013
		EP 2576431 A1	10-04-2013
		RU 2012156935 A	10-07-2014
		US 2011318251 A1	29-12-2011
		US 2014248205 A1	04-09-2014
		WO 2011150253 A1	01-12-2011

Information on Search Strategy - Pilot phase (see OJ 2015, A86)
The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number
PCT/EP2018/052358

TITLE: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

APPLICANT: CASALE SA

IPC CLASSIFICATION: C01B3/02, C01B3/36, C01C1/04

EXAMINER: Werner, Håkan

CONSULTED DATABASES:

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC: C01B3/025, C01C1/04, C01B3/36, C01B2203/0283, C01B2203/068

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:
ammonia syngas
natural gas
carbon dioxide
shift
carbon monoxide
hydrogen
air separation/ASU
oxygen
oxygen enriched

EPO FORM P04A42

Electronic Patent Application Fee Transmittal	
Application Number:	
Filing Date:	
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Filer:	Marcus S. Simon/Holly Morton
Attorney Docket Number:	283386WOUS01_495230-44
Filed as Small Entity	

Filing Fees for U.S. National Stage under 35 USC 371

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
BASIC NATIONAL STAGE FEE	2631	1	150	150
NATL STAGE SEARCH FEE - REPORT PROVIDED	2642	1	260	260
NATL STAGE EXAM FEE - ALL OTHER CASES	2633	1	380	380
Pages:				
Claims:				
CLAIMS IN EXCESS OF 20	2615	3	50	150
Miscellaneous-Filing:				
OATH/DECL > 30 MOS FROM 371 COMMENCEMENT	2617	1	70	70

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1010**

Electronic Acknowledgement Receipt	
EFS ID:	36862709
Application Number:	16485695
International Application Number:	PCT/EP2018/052358
Confirmation Number:	3128
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Customer Number:	116407
Filer:	Marcus S. Simon/Holly Morton
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	283386WOUS01_495230-44
Receipt Date:	13-AUG-2019
Filing Date:	
Time Stamp:	16:35:54
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1010
RAM confirmation Number	E20198CG57382764
Deposit Account	506181
Authorized User	Holly Morton
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.17 (Patent application and reexamination processing fees) 37 CFR 1.19 (Document supply fees)	

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

37 CFR 1.492 (National application filing, search, and examination fees)

37 CFR 1.492(a) (Basic national fee only)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Application Data Sheet	20190813_283386WOUS01_495230-44_ADS.pdf	1256195 298051151a96bca69dbb3deb594dd7328ea43e32	no	8
Warnings:					
Information:					
2	Power of Attorney	20190813_283386WOUS01_495230-44_PoA.pdf	511879 83d28756c599fa62b45009a40b0bb770716b6e06	no	2
Warnings:					
The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing					
Information:					
3	Miscellaneous Incoming Letter	20190813_283386WOUS01_495230-44_Transmittal.pdf	268636 372f4c4bdc63a80644ed1f799c43d6c05e9b5aeb	no	4
Warnings:					
Information:					
4		20190813_283386WOUS01_495230-44_PCTPublication.pdf	1520936 271ef227658f58efd1d9b723cc4c87ed50c9b48a	yes	42

Multipart Description/PDF files in .zip description

Document Description	Start	End
Abstract	1	2
Specification	3	34
Claims	35	38
Drawings-only black and white line drawings	39	42

Warnings:
Information:

5	Documents submitted with 371 Applications	20190813_283386WOUS01_495230-44_PCTNoticeOfTheRecordingOfAChange.pdf	250107 2b679007c14e3cacc0e2470ec92cba2d72c73590	no	1
Warnings:					
The page size in the PDF is too large. The pages should be 8.5 x 11 or A4. If this PDF is submitted, the pages will be resized upon entry into the Image File Wrapper and may affect subsequent processing					
Information:					
6	Documents submitted with 371 Applications	20190813_283386WOUS01_495230-44_IPRP.pdf	503389 fd6eaa7173df322faf503519f984f8fd731e4d58	no	13
Warnings:					
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Information:					
7	Documents submitted with 371 Applications	20190813_283386WOUS01_495230-44_ISR.pdf	142795 337b9d912c142a2bbc1406d7032e093951224c32	no	5
Warnings:					
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Information:					
8		20190813_283386WOUS01_495230-44_PreliminaryAmendment.pdf	42892 909d09ee25a736abf4e1745b3211890a4c37e8c3	yes	7

Multipart Description/PDF files in .zip description

Document Description	Start	End
Preliminary Amendment	1	1
Specification	2	2
Claims	3	6
Applicant Arguments/Remarks Made in an Amendment	7	7

Warnings:					
Information:					
9	Information Disclosure Statement (IDS) Form (SB08)	20190813_283386WOUS01_495230-44_IDS.pdf	37301 8a862425514b95604c1c67925129816f81d7b824	no	3

Warnings:					
Information:					
This is not an USPTO supplied IDS fillable form					
10	Foreign Reference	WO2010018550A1.pdf	3431970 3639b6c6aadb1d9bb3e58f3bd69acdefa20616f5	no	33
Warnings:					
Information:					
11	Non Patent Literature	IPRP_PCTEP2018052358_completed_20190510.pdf	1273274 b8d64a26926f815d15753afd6ad0d5926a0059f3	no	13
Warnings:					
Information:					
12	Non Patent Literature	ISR_PCTEP2018052358_mailed_20180731.pdf	352942 f431e1e041df9253994f70645e3af4185fe07d56	no	5
Warnings:					
Information:					
13	Fee Worksheet (SB06)	fee-info.pdf	38285 0b74b24df5913444142cf83aa7c7eedcdd0d89be	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	9630601		

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

New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

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

Secrecy Order 37 CFR 5.2:

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

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Francesco		Baratto	

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

City	Como	Country of Residence i	IT

Mailing Address of Inventor:

Address 1	Viale Varese 83		
Address 2			
City	Como	State/Province	
Postal Code	22100	Country i	IT

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Raffaele		Ostuni	

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

City	Lugano	Country of Residence i	CH

Mailing Address of Inventor:

Address 1	Via Montarina 21		
Address 2			
City	Lugano	State/Province	
Postal Code	6900	Country i	CH

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

Correspondence Information:

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

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

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

Customer Number	116407		
Email Address	ip.docket.slc@dorsey.com	Add Email	Remove Email

Application Information:

Title of the Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE		
Attorney Docket Number	28336WOUS01_495230-44	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	4	**Suggested Figure for Publication (if any)**	

Filing By Reference:

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

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

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

Publication Information:

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

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

Representative Information:

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

Please Select One:	● Customer Number	US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	116407		

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

Domestic Benefit/National Stage Information:

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

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	a 371 of international	PCT/EP2018/052358	2018-01-31

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

Foreign Priority Information:

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

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
17156256.4	EP	2017-02-15	

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
17195305.2	EP	2017-10-06	

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

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

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

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

Authorization or Opt-Out of Authorization to Permit Access:

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

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

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

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

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

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

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

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

Applicant Information:

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

Applicant 1 — Remove

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

Clear

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

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

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	CASALE SA		
Mailing Address Information For Applicant:			
Address 1	Via Pocobelli 6		
Address 2			
City	Lugano	**State/Province**	
Country	CH	Postal Code	6900
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

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

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

Assignee 1

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

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

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

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

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

Signature	/Marcus S. Simon, Reg.# 50258/			Date (YYYY-MM-DD)	2019-08-13
First Name	Marcus S.	Last Name	Simon	Registration Number	50258

Additional Signature may be generated within this form by selecting the Add button. Add

PTO/AIA/14 (02-18)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	

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

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1 The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

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

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

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

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

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

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

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

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

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82A (07-13)
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TRANSMITTAL FOR POWER OF ATTORNEY TO ONE OR MORE REGISTERED PRACTITIONERS

NOTE: This form is to be submitted with the Power of Attorney by Applicant form (PTO/AIA/82B) to identify the application to which the Power of Attorney is directed, in accordance with 37 CFR 1.5, unless the application number and filing date are identified in the Power of Attorney by Applicant form. If neither form PTO/AIA/82A nor form PTO/AIA82B identifies the application to which the Power of Attorney is directed, the Power of Attorney will not be recognized in the application.

Application Number	TBD
Filing Date	August 13, 2019
First Named Inventor	Francesco Baratto
Title	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE
Art Unit	TBD
Examiner Name	TBD
Attorney Docket Number	283386WOUS01_495230-44

SIGNATURE of Applicant or Patent Practitioner

Signature	/Marcus S. Simon, Reg.# 50258/	Date (Optional)	August 13, 2019
Name	Marcus S. Simon	Registration Number	50258
Title (if Applicant is a juristic entity)	Attorney for Applicant		
Applicant Name (if Applicant is a juristic entity)	Casale SA		

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ *Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: PA..
Document Description: Power of Attorney

PTO/AIA/82B (07-13)
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POWER OF ATTORNEY BY APPLICANT

I hereby revoke all previous powers of attorney given in the application identified in either the attached transmittal letter or the boxes below.

Application Number	Filing Date

(Note: The boxes above may be left blank if information is provided on form PTO/AIA/82A.)

☑ I hereby appoint the Patent Practitioner(s) associated with the following Customer Number as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above: 116407

OR

☐ I hereby appoint Practitioner(s) named in the attached list (form PTO/AIA/82C) as my/our attorney(s) or agent(s), and to transact all business in the United States Patent and Trademark Office connected therewith for the patent application referenced in the attached transmittal letter (form PTO/AIA/82A) or identified above. (Note: Complete form PTO/AIA/82C.)

Please recognize or change the correspondence address for the application identified in the attached transmittal letter or the boxes above to:

☑ The address associated with the above-mentioned Customer Number

OR

☐ The address associated with Customer Number:

OR

☐ Firm or Individual Name					
Address					
City		State		Zip	
Country					
Telephone		Email			

I am the Applicant (if the Applicant is a juristic entity, list the Applicant name in the box):

Casale SA

☐ Inventor or Joint Inventor (title not required below)

☐ Legal Representative of a Deceased or Legally Incapacitated Inventor (title not required below)

☑ Assignee or Person to Whom the Inventor is Under an Obligation to Assign (provide signer's title if applicant is a juristic entity)

☐ Person Who Otherwise Shows Sufficient Proprietary Interest (e.g., a petition under 37 CFR 1.46(b)(2) was granted in the application or is concurrently being filed with this document) (provide signer's title if applicant is a juristic entity)

SIGNATURE of Applicant for Patent

The undersigned (whose title is supplied below) is authorized to act on behalf of the applicant (e.g., where the applicant is a juristic entity).

Signature		Date (Optional)	
Name	Federico Zardi Sergio Bebernardi		
Title	CEO COO		

NOTE: Signature - This form must be signed by the applicant in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. If more than one applicant, use multiple forms.

☑ Total of 1 forms are submitted.

This collection of information is required by 37 CFR 1.131, 1.32, and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO-1390 (01-18)
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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371

Attorney Docket No.	U.S. Application No. (if known, see 37 CFR 1.5)
283386WOUS01_495230-44	

International Application No.	International Filing Date	Priority Date Claimed
PCT/EP2018/052358	January 31, 2018	February 15, 2017

Title of Invention
PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

First Named Inventor
Fransesco Baratto

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). NOTE: The express request under 35 U.S.C. 371(f) will not be effective unless the requirements under 35 U.S.C. 371(c)(1), (2), and (4) for payment of the basic national fee, copy of the International Application and English translation thereof (if required), and the oath or declaration of the inventor(s) have been received.
2. ■ A copy of the International Application (35 U.S.C. 371(c)(2)) is attached hereto (not required if the International Application was previously communicated by the International Bureau or was filed in the United States Receiving Office (RO/US)).
3. An English language translation of the International Application (35 U.S.C. 371(c)(2))
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
4. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))
   a. ☐ is attached.
   b. ☐ was previously filed in the international phase under PCT Rule 4.17(iv).

Items 5 to 8 below concern amendments made in the international phase.

PCT Article 19 and 34 amendments

5. ☐ Amendments to the claims under PCT Article 19 are attached (not required if communicated by the International Bureau) (35 U.S.C. 371(c)(3)).
6. ☐ English translation of the PCT Article 19 amendment is attached (35 U.S.C. 371(c)(3)).
7. ☐ English translation of annexes (Article 19 and/or 34 amendments only) of the International Preliminary Examination Report is attached (35 U.S.C. 371(c)(5)).

Cancellation of amendments made in the international phase

8a. ☐ Do not enter the amendment made in the international phase under PCT Article 19.

8b. ☐ Do not enter the amendment made in the international phase under PCT Article 34.

NOTE: A proper amendment made in English under Article 19 or 34 will be entered in the U.S. national phase application absent a clear instruction from applicant not to enter the amendment(s).

The following items 9 to 17 concern a document(s) or information included.

9. ■ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
10. ■ A preliminary amendment.
11. ■ An Application Data Sheet under 37 CFR 1.76.
12. ☐ A substitute specification. NOTE: A substitute specification cannot include claims. See 37 CFR 1.125(b).
13. ■ A power of attorney and/or change of address letter.
14. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13*ter*.3 and 37 CFR 1.821-1.825 (not required if sequence listing in text format was indicated on the PCT Request as part of the International Application and the sequence listing was published as part of the international application).
15. ☐ Assignment papers *(cover sheet and document(s))*. Name of Assignee: _____
16. ☐ 37 CFR 3.73(c) Statement *(when there is an Assignee)*.

This collection of information is required by 37 CFR 1.414 and 1.491-1.492. The information is required to obtain or retain a benefit by the public, which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 15 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop PCT, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

PTO-1390 (01-18)
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U.S. APPLN. No. (if known – see 37 CFR 1.5)	INTERNATIONAL APPLICATION No.	ATTORNEY DOCKET No.
	PCT/EP2018/052358	283386WOUS01_495230-44

17. [X] Other items or information:

PCT Notification of the Recording of a Change mailed July 25, 2018. International Search Report from International Application No. PCT/EP2018/052358 mailed July 31, 2018. International Preliminary Report on Patenability for International Application No. PCT/EP2018/052358 completed May 10, 2019.

The following fees have been submitted.	CALCULATIONS
18. [■] Basic national fee (37 CFR 1.492(a)) **$300**	$ 300
19. [■] Examination fee (37 CFR 1.492(c)) • If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4)..... **$0** • All other situations **$760**	$ 760
20. [■] Search fee (37 CFR 1.492(b)) • If the written opinion prepared by ISA/US or the international preliminary examination report prepared by IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4)..... **$0** • Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority ..... **$140** • International Search Report prepared by an ISA other than the US and provided to the Office or previously communicated to the US by the IB..... **$520** • All other situations **$660**	520 $
TOTAL OF 18, 19, and 20 =	$ 1580
[ ] Additional fee for specification and drawings filed in paper over 100 sheets (excluding sequence listing in compliance with 37 CFR 1.821(c) or (e) in an electronic medium or computer program listing in an electronic medium) (37 CFR 1.492(j)). Fee for each additional 50 sheets of paper or fraction thereof **$400**	

Total Sheets	Extra Sheets	Number of each additional 50 or fraction thereof (round **up** to a whole number)	RATE	
- 100 =	/ 50 =		x **$400**	$

Surcharge for furnishing any of the search fee, examination fee, or the oath or declaration after the date of commencement of the national stage (37 CFR 1.492(h))..... **$140**	$ 140

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	23 - 20 =	3	x **$100**	$ 300
Independent claims	- 3 =		x **$460**	$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			**+ $820**	$

Fee for submission of Sequence Listing text file of 300 MB to 800 MB (37 CFR 1.21(o)(1))..... **$1,000**	$
Fee for submission of Sequence Listing text file of more than 800 MB (37 CFR 1.21(o)(2))..... **$10,000**	$
Processing fee for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i))..... **$140 +**	$
TOTAL OF ABOVE CALCULATIONS =	$ 2020
[■] **Applicant asserts small entity status.** See 37 CFR 1.27. Fees above are reduced by ½.	
[ ] **Applicant certifies micro entity status.** See 37 CFR 1.29. Fees above are reduced by ¾. Applicant must attach form PTO/SB/15A or B or equivalent.	
TOTAL NATIONAL FEE =	$ 1010
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31)..... **$50.00** per property **+**	$
TOTAL FEES ENCLOSED =	$ 1010

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a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees.

c. ☒ The Director is hereby authorized to charge additional fees which may be required, or credit any overpayment, to Deposit Account No. 506181 as follows:

i. ☒ any required fee.

ii. ☐ any required fee except for excess claims fees required under 37 CFR 1.492(d) and (e) and multiple dependent claim fee required under 37 CFR 1.492(f).

d. ☒ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. The PTO-2038 should only be mailed or faxed to the USPTO. However, when paying the basic national fee, the PTO-2038 may NOT be faxed to the USPTO.

ADVISORY: If filing by EFS-Web, do **NOT** attach the PTO-2038 form as a PDF along with your EFS-Web submission. Please be advised that this is **not** recommended and by doing so your **credit card information may be displayed via PAIR**. To protect your information, it is recommended to pay fees online by using the electronic payment method.

NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the International Application to pending status.

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

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013, and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.

NOTE 1: By providing this statement under 37 CFR 1.55 or 1.78, **this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA**.

NOTE 2: A U.S. national stage application may not claim priority to the international application of which it is the national phase. The filing date of a U.S. national stage application is the international filing date. See 35 U.S.C. 363.

Correspondence Address

☒ The address associated with Customer Number: 116407 **OR** ☐ Correspondence address below

Name					
Address					
City		State		Zip Code	
Country		Telephone			
Email					

Signature	/Marcus S. Simon, Reg.# 50258/	Date	August 13, 2019
Name (Print/Type)	Marcus S. Simon	Registration No. (Attorney/Agent)	50258

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PATENT COOPERATION TREATY

PCT/EP2018/052358

RICEVUTO

30 LUG 2018

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

ZARDI, Marco
c/o M. ZARDI & Co SA
Via Pioda, 6
6900 Lugano

Date of mailing *(day/month/year)*
25 July 2018 (25.07.2018)

Applicant's or agent's file reference
AMC121BWO

IMPORTANT NOTIFICATION

International application No.
PCT/EP2018/052358

International filing date *(day/month/year)*
31 January 2018 (31.01.2018)

1. The following indications appeared on record concerning:

☐ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address
BARATTO, Francesco
Via Borgo Vico, 127
22100 Como
Italy

State of Nationality | State of Residence

Telephone No.

Facsimile No.

E-mail address

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address
BARATTO, Francesco
Viale Varese 83
22100 Como
Italy

State of Nationality | State of Residence

Telephone No.

Facsimile No.

E-mail address
☐ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☒ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☒ the International Preliminary Examining Authority
☐ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 70 80

Authorized officer
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e-mail pct.team5@wipo.int
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Form PCT/IB/306 (January 2009)

1/R9A52WWQ9FVYV0

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AMC121BWO	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/EP2018/052358	International filing date *(day/month/year)* 31.01.2018	Priority date *(day/month/year)* 15.02.2017
International Patent Classification (IPC) or national classification and IPC INV. C01B3/02		
Applicant Casale SA		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 7 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions).
      ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2).
      ☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)).
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in the form of an Annex C/ST.25 text file, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*ter* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11.06.2018	10.05.2019
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	Authorized officer Werner, Håkan Telephone No. +49 89 2399-8571

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Box No. I Basis of the report

1. With regard to the **language**, this report is based on

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3(a) and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4(a))
   - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-32 as originally filed

Claims, Numbers

1-16 filed with telefax on 14-01-2019

Drawings, Sheets

1-4 as originally filed

☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-*bis*)):
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

5. ☐ This report has been established:
   - ☐ taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-*bis*) and 70.2(e)).
   - ☐ without taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91(Rules 66.4*bis* and 70.2(e)).

6. ☒ With regard to top-up searches (Rules 66.1*ter* and 70.2(f)):
   ☒ A top-up search was carried out by this Authority on 23.04.2019 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
   ☐ Additional relevant documents have been discovered during the top-up search.
   ☐ No top-up search was carried out by this Authority because it would serve no useful purpose.

7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

* *If item 4 applies, some or all of those sheets may be marked "superseded".*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-14
	No:	Claims	15, 16
Inventive step (IS)	Yes:	Claims	1-14
	No:	Claims	15, 16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

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SECTION V

1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 15 and 16 is not new in the sense of Article 33(2) PCT.

2 D1 discloses (in particular paragraphs [0023]-[0027], [0031], [0032] and [0034] and Figs. 2 and 3) a method for making ammonia comprising reforming natural gas using a gas comprising 90% oxygen from an ASU. The syngas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a coldbox whereby two streams are obtained. One stream is sent to the ammonia converter and the other stream is used as fuel in the primary reformer. Before the CO_2 depleted syngas is treated in a coldbox it is treated in a methanator. Therefore, the depleted syngas will inevitably have an amount of CO_2 < 1000ppm. The tail gas (=CO_2 depleted syngas used as fuel gas) can be compressed followed by expansion (paragraph [0031]). D1 further disclosed that existing ammonia plants can be revamped using the means disclosed in D1, namely an ASU and a coldbox with which two streams are obtained, one which is sent to the ammonia converter and the other which is used as fuel in the primary reformer.

3 Therefore, the subject-matter of claims 15 and 16 is not new vis-a-vis D1.

4 The subject-matter of claims 1-14 relates to new and inventive matter (Article 33(2) and (3) PCT).

5 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses (in particular paragraphs [0023]-[0027], [0031], [0032] and [0034] and Figs. 2 and 3) a method for making ammonia comprising reforming natural gas using a gas comprising 90% oxygen from an ASU. The syngas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a coldbox whereby two streams are obtained, a fuel stream comprising methane, H2 and N2 and a syngas stream comprising N2 and H2 in a ratio of 1:3. The syngas stream is sent to the ammonia converter and the fuel stream is used as fuel in the primary reformer.

6 The subject-matter of claim 1 therefore differs from this known process in that the two streams obtained have the same composition and is therefore new (Article 33(2) PCT).

7 The problem to be solved by the present invention may be regarded as reducing the CO2 emission from the plant.

8 The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons: Using part of the CO2 depleted syngas as fuel in a furnace in the process reduces the CO2 emission of the process. There is no hint in the prior art this solution to the problem.

9 Claims 2-14 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

10 Further documents cited in the search report:

D2 discloses a method for making syngas. Natural gas is reformed whereby a synthesis gas is obtained. The synthesis gas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a PSA unit where a H2 rich stream and a residual stream are obtained. The residual stream comprising H2 is used as fuel in the primary reformer. With this method enhanced CO_2 recovery during steam reforming can be obtained.

D3 discloses a method for making ammonia and urea with reduced CO_2 emission. A synthesis gas is produced using oxygen from an ASU. CO in the obtained syngas is converted into CO_2. Then CO_2 is removed from the syngas with now comprises H_2. The CO_2 depleted synthesis gas is combined with N_2 from the ASU whereby ammonia is obtained. Ammonia is reacted with CO_2 whereby urea is produced. Using part of the CO_2 depleted syngas as fuel is not disclosed.

ZARDI

EUROPEAN PATENT AND TRADEMARK ATTORNEYS

EPO
EUROPEAN PATENT OFFICE
International Preliminary Examining Authority
D-80298 Munich
Germany

BY FAX (11 pages) AND MAIL

Lugano, January 14, 2019

Your file:
Our file: **AMC121BWO**

Re: International Patent Application No. **PCT/EP2018/052358**

Applicant: CASALE S.A.

Authorized Officer: W HÅKAN

Dear Sirs,

In response to the Written Opinion of the International Searching Authority pursuant to Rule 43*bis*.1 PCT dated July 31, 2018 the Applicant wishes to submit the following amendments and the following observations.

AMENDMENTS

In the claims:

Claim 1 as originally filed has been amended by inserting therein the features of dependent claim 2. Claims 2 and 16 have been deleted and the other claims renumbered accordingly.

A new set of claims 1-16 is enclosed to the present letter, which should replace the claims as originally filed, together with a copy of original claims 1-18 with hand-written amendments.

OBSERVATIONS

1. Re Item V of the Written Opinion

In the Applicant's opinion, the subject-matter of independent claim 1 should be regarded as new and inventive over the cited prior art documents D1 (US2004/0234426), D2 (WO 2010/018500), D3 (US 2015/0031916) and D4 (US 2014/0248205) for the following reasons.

In none of D1, D2 and D4 the stream fed as a fuel to the furnace is separated of a part of a CO2-depleted synthesis gas, as recited in the characterizing portion of present claim 1.

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In all these prior art documents, such a fuel stream is instead obtained through a purification step, either cryogenic or through PSA, of such a CO2 depleted synthesis gas. In other words, the fuel stream is not a stream, which is merely split from a CO2 depleted synthesis gas, as in present claim 1, but - on the contrary - it is a purge stream resulting as a by-product from the transformation process of a CO2 depleted synthesis gas into a purified synthesis gas.

Indeed, in D1, D2 and D4, the purge stream used as a fuel and the purified synthesis gas stream are not comparable the one to the other, having substantially different composition.

The subject-matter of present claim 1 thus differs from the processes of D1, D2 and D4 at least by the features recited in its characterizing portion.

Actually, the processes disclosed in these prior art documents suffer of the same drawbacks as set forth in the prior art section of the present application (see for instance page 2, lines 20-25).

As to D3, it is noted that this document cannot be regarded as relevant prior art with respect to the present invention. For sure, this document cannot be regarded as the closest prior art in connection with the claimed process.

According to the invention, a process for synthesis of ammonia from natural gas is claimed.

On the contrary in D3, gasification of waste is disclosed and taught. See for instance D3, par. [0025]. By waste reference is made to domestic waste and organic waste. See for instance D3, par. [0001], [0007]-[0009]. This has nothing to do nor can it be confused with or compared to the technical field of the present invention.

The skilled person of ammonia synthesis from natural gas would have never considered a document related to the disposal of domestic or organic waste (i.e. a document belonging to a far remote technical field) in the absence of a clear and unambiguous hint in the prior art to do so. Hint, which is however totally missing. In this regard, any assertion to the contrary should be traversed for hindsight.

In any case, even supposing – *arguendo* – to combine D3 with D1, D2 or D4, the skilled person would have still not being able to arrive in an obvious manner to the claimed process since the features recited in the characterizing section of claim 1 would have still been missing.

In summary, in view of the above-identified distinguishing features the technical problem underlying the present invention should be regarded as the one set forth in the description at page 2, line 27 to page 3, line 1. The skilled person aiming to solve such a technical problem, by considering the available prior art documents would have not been directed in an obvious manner towards the claimed process, the latter being only possible with the exercise of an inventive skill.

Any assertion stating that the subject-matter of claim 1 is obvious to the skilled person without any prior art substantiation should be traversed as being the result of an inadmissible ex-post facto analysis of the invention.

Therefore, the subject-matter of claim 1 should be regarded as new and also involving an inventive step in view of D1-D4 (Art. 33(2)(3) PCT).

The above observations also apply to the independent claim 15 as well as to the dependent claims 2-14 and 16.

In connection with claim 15, it is noted that the current wording of: separating a part of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion, gives no doubt about the fact that the separation takes place in the same manner as recited in claim 1 and can thus not be confused with or compared to the purification step of the prior art (see also present description, page 4, line 27 to page 5, line 3).

*** * ***

CONCLUSIONS

In consideration of the above arguments, the Applicant is of the opinion that the subject-matter of present claims 1-16 meets the requirements of patentability.

We therefore look forward to receiving a favorable International Preliminary Examination Report; however, should the Authorized Officer be of a different opinion, he is kindly requested to issue a further Written Opinion or to contact the undersigned for a telephone or personal interview according to Article 34(2)(a) and Rule 66.6 PCT.

Respectfully submitted.

The Representative
Marco Zardi
c/o M. ZARDI & Co.

Encl.: as above

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CLAIMS

1) Process for synthesis of ammonia from natural gas, comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas (11) containing hydrogen, CO and CO2, in a conversion section;

a treatment of said synthesis gas (11) comprising at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas (12) and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas,

characterized by:

separation of a part (14) of said CO2-depleted synthesis gas (12) as fuel fraction, wherein said fuel fraction (14) is fed as fuel to at least one furnace and wherein said separation of the fuel fraction comprises the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia, optionally after further purification.

2) Process according to claim 1, wherein said fuel fraction (14) is comprised between 1% and 40% of the total amount of said CO2-depleted syngas (12), preferably between 10% and 30%.

3) Process according to any one of the preceding claims, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

4) Process according to any one of the preceding claims, wherein said CO2-

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uration: 01.14.2019 08:06:55 PM - 01.14.2019 08:10:04 PM. This page 4 of 11 was completed at 01.14.2019 08:08:15 PM

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depleted syngas (12) contains no more than 1000 ppm by volume of CO2.

5) Process according to any one of the preceding claims, wherein said enriched air contains at least 50% of oxygen, preferably at least 90% oxygen.

6) Process according to any one of the preceding claims, wherein said fuel fraction (14) of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

7) Process according to any one of the preceding claims, wherein: a purge gas (21) of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in it, obtaining a hydrogen-rich gas (20) and a tail gas (15) containing methane; at least part (15a) of said tail gas (15) is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

8) Process according to any one of the preceding claims, wherein: a part of said CO2-depleted syngas (12) is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, preferably all of it, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

9) Process according to any one of the preceding claims, also comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas (12), optionally after heating it.

10) Process according to any one of the preceding claims, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0, preferably greater than 2.4 and more preferably greater than 2.7.

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uration: 01.14.2019 08:06:55 PM - 01.14.2019 08:10:04 PM. This page 5 of 11 was completed at 01.14.2019 08:08:32 PM

11) Process according to any one of the preceding claims, wherein

said synthesis gas fuel fraction (14) forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

12) Process according to any one of the preceding claims, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

13) Process according to any one of the preceding claims, wherein:

the conversion of the natural gas charge into synthesis gas comprises a step of autothermal reforming, optionally with pre-reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

14) Process according to any one of the preceding claims, wherein the conversion of the natural gas into synthesis gas comprises: primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

15) Method for revamping a plant for the synthesis of ammonia from natural gas or ammonia/urea plant, wherein

the plant comprises a reforming section which includes a primary steam

Received at the EPO on Jan 14, 2019 20:10:04. Page 6 of 11 14/01/2019
Duration: 01.14.2019 08:06:55 PM - 01.14.2019 08:10:04 PM. This page 6 of 11 was completed at 01.14.2019 08:08:50 PM

reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by means of a shift reaction of carbon monoxide into carbon dioxide, decarbonation and optionally methanation.

and the revamping method comprises at least:

providing a flow (22) of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part (14) of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction (14) of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

16) Method for revamping according to claim 15 comprising: installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
AMC121BWO		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP2018/052358	31 January 2018 (31-01-2018)	15 February 2017 (15-02-2017)
Applicant		
CASALE SA		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language,** the international search was carried out on the basis of:
      [X] the international application in the language in which it was filed
      [ ] a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. [ ] This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. [ ] **Certain claims were found unsearchable** (See Box No. II)

3. [ ] **Unity of invention is lacking** (see Box No III)

4. With regard to the **title,**
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   [X] the text is approved as submitted by the applicant
   [ ] the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings,**
   a. the figure of the **drawings** to be published with the abstract is Figure No. 1
      [X] as suggested by the applicant
      [ ] as selected by this Authority, because the applicant failed to suggest a figure
      [ ] as selected by this Authority, because this figure better characterizes the invention
   b. [ ] none of the figures is to be published with the abstract

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/052358

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/02 C01B3/36 C01C1/04
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)
C01B C01C

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, CHEM ABS Data, 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	US 2004/234426 A1 (REDDY SATISH [US] ET AL) 25 November 2004 (2004-11-25)	1,3,5-8, 10,14-18
A	paragraphs [0023] - [0027], [0031], [0032], [0034]; figures 2,3	2,4,9, 11-13
Y	WO 2010/018550 A1 (AIR LIQUIDE [FR]; VAKIL TARUN D [US]; WOLF ULRICH [DE]) 18 February 2010 (2010-02-18)	1,3-7, 11,12, 15-18
A	page 3, line 23 - page 4, line 19; claim 7; figures 2,3 page 11, line 20 - page 12, line 8 page 17, lines 15-27	2,8-10, 13,14
Y	US 2015/031916 A1 (KISS GUENTER HANS [CH]) 29 January 2015 (2015-01-29)	1,3-7, 11,12, 14-18
A	paragraphs [0012] - [0020]; figure 1	2,8-10, 13

-/--

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 July 2018	31/07/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Werner, Håkan

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Form PCT/ISA/210 (second sheet) (April 2005)

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/052358

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2014/248205 A1 (ALLAM RODNEY J [GB]) 4 September 2014 (2014-09-04) paragraphs [0021], [0022], [0034] - [0038]; figure 2 -----	1,7,14

3

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/052358

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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Information on Search Strategy - Pilot phase (see OJ 2015, A86)
The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number
PCT/EP2018/052358

TITLE: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

APPLICANT: CASALE SA

IPC CLASSIFICATION: C01B3/02, C01B3/36, C01C1/04

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natural gas
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carbon monoxide
hydrogen
air separation/ASU
oxygen
oxygen enriched

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Bescheinigung	Certificate	Attestation
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Patentanmeldung Nr.	**Patent application No.**	**Demande de brevet n°**
	17156256.4 / EP17156256	

The organization code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP17156256.

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le President de l'Office européen des brevets
p.o.

V. Joseph

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Anmeldung Nr:
Application no.: 17156256.4
Demande no :

Anmeldetag:
Date of filing: 15.02.17
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Anmelder / Applicant(s) / Demandeur(s):

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Bezeichnung der Erfindung / Title of the invention / Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, oder falls die Anmeldung in einer Nicht-Amtssprache des EPA eingereicht wurde, siehe Beschreibung bezüglich ursprünglicher Bezeichnung.
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In Anspruch genommene Priorität(en) / Priority(Priorities) claimed / Priorité(s) revendiquée(s)
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Processo per la sintesi dell'ammoniaca a basse emissioni in atmosfera di CO2

Campo di applicazione

L'invenzione riguarda il settore degli impianti per la sintesi dell'ammoniaca alimentati a gas naturale (NG).

Arte nota

Gli impianti per la sintesi dell'ammoniaca del tipo qui considerato prevedono una sezione atta a convertire il gas naturale in un gas di make-up contenente idrogeno e azoto, e una sezione di sintesi in cui detto gas di make-up reagisce cataliticamente ad alta pressione per dare ammoniaca.

La sezione che genera detto gas di make-up è detta in gergo tecnico front-end. Si usa invece il termine back-end per indicare la sezione di sintesi dell'ammoniaca e la rispettiva sezione frigorifera dedicata a raffreddare l'effluente della sezione di sintesi per poter separare l'ammoniaca.

Nel front-end, il gas naturale desolforato è sottoposto a reforming ottenendo un gas contenente essenzialmente idrogeno, monossido di carbonio CO, diossido di carbonio CO2. Detto gas è in seguito sottoposto a reazione di shift che converte CO in CO2; rimozione di CO2 (decarbonatazione) e preferibilmente metanazione.

Il processo di reforming, in un tipo comune di impianti, prevede un reforming primario con vapore e un successivo reforming secondario catalitico con aria (air-fired). Il reformer primario è riscaldato da bruciatori che utilizzano, quale combustibile, una parte del gas naturale disponibile. Nel reformer secondario invece l'effluente del primario brucia grazie al contatto con l'ossigeno contenuto nell'aria. In alcuni impianti si utilizzano altre configurazioni di

reforming, per esempio un reformer autotermico (ATR) preceduto da un forno di riscaldo della carica, cioè della miscela gassosa alimentata a detto reformer.

I descritti impianti ammoniaca hanno notevoli emissioni di CO2 in atmosfera, complessivamente dell'ordine di 100 milioni di tonnellate di CO2 all'anno. Una delle fonti principali di emissione di CO2 è rappresentata dai fumi di combustione del reformer primario e di eventuali altri forni bruciatori, per esempio riscaldatori ausiliari.

Per ragioni ambientali, occorre minimizzare le emissioni di CO2 dai fumi degli impianti NH3. Il problema affligge in particolare gli impianti ammoniaca più datati che sono meno efficienti dei nuovi e hanno maggiori emissioni di CO2 a camino in rapporto alla quantità di ammoniaca prodotta. È altresì necessario che la riduzione delle emissioni non aumenti troppo il costo di produzione dell'ammoniaca.

Allo stato dell'arte, però, i processi per la cattura di CO2 da fumi si basano su lavaggio con solventi (ad es. il solvente KS-1™ di Mitsubishi). I relativi impianti sono costosi e complicati, hanno un alto consumo energetico, necessitano del solvente che è costoso. Pertanto questi processi di cattura della CO2 non sono applicabili negli impianti qui considerati dato che alzerebbero troppo il costo di produzione dell'ammoniaca.

Sommario dell'invenzione

Lo scopo dell'invenzione è di mettere a disposizione una tecnica per realizzare processi di sintesi dell'ammoniaca con emissioni di CO2 in atmosfera fortemente ridotte rispetto all'arte nota. Un altro scopo dell'invenzione è di mettere a disposizione una tecnica per ammodernare gli impianti esistenti, del tipo con reformer secondario alimentato ad aria, in grado di ridurre drasticamente le emissioni di CO2 in atmosfera.

Gli scopi sono raggiunti con un processo e con un metodo di ammodernamento (revamping) secondo le rivendicazioni.

Secondo l'invenzione, un processo di sintesi dell'ammoniaca da gas naturale comprende:

conversione di una carica di gas naturale desolforato e vapore, con aria arricchita in ossigeno o con ossigeno, a formare un gas di sintesi contenente idrogeno, CO e CO2;

un trattamento di detto gas di sintesi comprendente almeno una reazione di shift del monossido di carbonio in CO2, e successiva separazione di CO2 dal gas, così ottenendo un gas di sintesi a ridotto contenuto di CO2 e una corrente gassosa ricca di CO2, contenente il CO2 separato dal gas;

opzionalmente, una fase di metanazione del gas di sintesi e/o una aggiunta di azoto al gas di sintesi, ottenendo un gas di make-up contenente azoto e idrogeno in opportuno rapporto molare per la sintesi di ammoniaca,

caratterizzato dal fatto che

una parte di detto gas di sintesi a ridotto contenuto di CO2 è separata a formare una quota combustibile del gas di sintesi, e detta quota combustibile è alimentata come combustibile a almeno un forno.

L'invenzione ha per oggetto anche un metodo di ammodernamento di un impianto originariamente comprendente una sezione di reforming che include un reformer primario con vapore e reformer secondario ad aria (air-fired), e trattamento del gas di sintesi comprendente shift di monossido di carbonio in diossido di carbonio, decarbonatazione e eventualmente metanazione. Il metodo di ammodernamento comprende almeno:

fornire una corrente di aria arricchita, o di ossigeno, e utilizzare detta corrente quale ossidante per il reformer secondario al posto dell'aria;

separare una quota parte del gas di sintesi a valle della decarbonatazione,

alimentare detta parte del gas di sintesi, avente un ridotto contenuto di CO2, come combustibile per almeno un forno dell'impianto.

Con il termine di forno si intende un apparecchio tra: un reformer a vapore (steam reformer) o un preriscaldatore della carica o un generatore di vapore o un surriscaldatore di vapore. Questi apparecchi, che operano con una combustione, sono identificati con il termine "fired heater". Detto forno in alcune realizzazioni è parte della sezione di conversione del gas naturale in gas di sintesi. Negli impianti combinati ammoniaca-urea detto forno può essere parte della sezione urea.

La parte di gas di sintesi separata, e inviata a detto almeno un forno, è definita quota di combustibile (quota fuel) del gas disponibile dopo la fase di shift. Preferibilmente detta quota fuel è compresa tra 1% e 40% del gas disponibile, più preferibilmente tra 10% e 30% e ancora più preferibilmente tra 20% e 30%. Per esempio in una realizzazione preferita la quota fuel è pari al 30%. La restante parte, che è destinata alla conversione in ammoniaca, è denominata quota di processo.

Si deve notare che detta quota fuel è relativamente alta, per esempio circa 1/3 del totale. L'invenzione infatti prevede di destinare a combustibile una porzione non trascurabile di gas di sintesi, per ridurre le emissioni di CO2. Ciò comporta la necessità di produrre una quantità aggiuntiva di gas di sintesi ma, come sarà meglio spiegato nel seguito con l'aiuto degli esempi, questa necessità è compensata dai vantaggi dell'invenzione.

Detta quota fuel è separata preferibilmente prima (a monte di) detta fase di metanazione se previste. Se è prevista una aggiunta di azoto, la quota fuel è separata prima di detta aggiunta di azoto.

La metanazione serve per rendere il gas adatto alla sintesi dell'ammoniaca, a valle della decarbonatazione; converte CO e CO2 residui in CH4, consumando H2, in accordo alle reazioni CO + 3H2 → CH4 + H2O e CO2 + 4H2 → CH4 + 2H2O.

La metanazione pertanto lascia una piccola quantità di metano nel gas di sintesi (slip di metano). La presenza di dette piccole quantità di metano nel gas di sintesi non è un problema ai fini della produzione dell'ammoniaca essendo il metano inerte nei confronti della reazione di sintesi. Tuttavia usando il gas di sintesi come combustibile, il metano in esso contenuto rappresenta una sorgente di CO2, sebbene di piccola entità.

In alcune realizzazioni dell'invenzione, per ridurre anche questa fonte di CO2 (cioè le emissioni dovute a slip di metano nel gas di sintesi) il processo comprende una purificazione catalitica atta a convertire selettivamente il CO a CO2 a monte della decarbonatazione. Una conversione selettiva del monossido di carbonio per esempio è ottenibile con il processo noto come Selectoxo™ che opera con la reazione CO + 1/2 O2 → CO2. L'ossigeno per l'ossidazione selettiva del CO può essere una parte della menzionata corrente di aria arricchita o ossigeno.

Un vantaggio di detta conversione selettiva è che il CO residuo dallo shift è convertito in CO2 e rimosso nella decarbonatazione. Di conseguenza la eventuale metanazione riguarda solo la quantità di CO2 residua dopo la fase di decarbonatazione e genera meno metano nel gas di sintesi.

Il menzionato gas di sintesi a ridotto contenuto di CO2 (CO2-depleted syngas) preferibilmente contiene non più di 1000 ppm in volume (0.1%) di CO2. Detto

gas è composto essenzialmente da idrogeno (H_2) con eventuali piccole quantità residue di CO e di CH4, tipicamente meno di 2% in volume e preferibilmente meno di 1%.

La combustione di detto gas è sostanzialmente libera da produzione di CO2. Infatti la combustione dell'idrogeno non forma CO2, e solo la piccola quantità di CO o di CH4, eventualmente presente, può formare CO2.

L'invenzione suggerisce di utilizzare una parte di gas di processo come combustibile per uno o più forni della sezione di reforming, contrariamente all'arte nota che, a questo scopo, utilizza parte del gas naturale, cioè un idrocarburo. Questa parte di gas di processo (quota fuel) è separata opportunamente dopo un trattamento di rimozione di CO2 e, come spiegato più sopra, contiene essenzialmente idrogeno che può bruciare senza formare CO2. Di conseguenza si comprende che l'invenzione consente di ridurre drasticamente le emissioni di CO2 in atmosfera.

Detta aria arricchita in ossigeno preferibilmente contiene almeno il 50% di ossigeno in volume e più preferibilmente almeno il 90% di ossigeno in volume e ancora più preferibilmente almeno il 95%. I vantaggi di un elevato contenuto di ossigeno nell'aria arricchita sono: maggiore potere calorifico del gas di sintesi; minore portata di gas di scarico (flue gas) a camino; minore portata volumetrica attraverso gli apparecchi della sezione di conversione e, di conseguenza, apparecchi più piccoli.

In alcune realizzazioni la fase di conversione del gas naturale in gas di sintesi comprende un reforming autotermico catalitico (ATR), opzionalmente preceduto da un reforming preliminare (pre-reforming). Vantaggiosamente in queste realizzazioni almeno una parte della quota fuel di gas di sintesi alimenta un forno di pre-riscaldo del gas prima del reforming autotermico.

In alcune realizzazioni la fase di conversione del gas naturale in gas di sintesi comprende una fase di ossidazione parziale non catalitica (POX). Vantaggiosamente in queste realizzazioni almeno una parte della quota fuel di gas di sintesi alimenta un forno di pre-riscaldo del gas prima della ossidazione parziale oppure per generazione di vapore o surriscaldamento di vapore.

In alcune realizzazioni la fase di conversione del gas naturale in gas di sintesi comprende una fase di reforming con vapore (steam reforming). Vantaggiosamente in queste realizzazioni almeno una parte della quota fuel di gas di sintesi alimenta i bruciatori del reformer.

Una parte della quota fuel può essere destinata, in alcune realizzazioni, a forni per la produzione e/o surriscaldo di vapore.

Ulteriori caratteristiche preferite sono le seguenti.

Generalmente nei processi ammoniaca si estrae dal processo (loop) di sintesi dell'ammoniaca un gas di spurgo, al fine di rimuovere gli inerti dal loop di sintesi, e detto gas di spurgo è trattato con un processo di recupero dell'idrogeno in esso contenuto (HRU). Detto processo di recupero genera un gas ricco di idrogeno che può essere riutilizzato per la sintesi, e un gas di coda (tail gas) contenente la maggior parte del metano inizialmente contenuto nel gas di spurgo. Normalmente detto gas di coda, dato il suo contenuto relativamente alto di metano, è usato esclusivamente come combustibile. Questo utilizzo del gas di coda tuttavia genera emissioni di CO2.

Un aspetto dell'invenzione prevede di riciclare almeno una parte di detto gas di coda come gas di processo nella fase di conversione del gas naturale, ad esempio nella fase di reforming o parziale ossidazione. Un vantaggio connesso è una ulteriore diminuzione delle emissioni di CO2.

In alcune realizzazioni una parte del detto gas di sintesi a ridotto contenuto di CO2 è trattata in un'unità per separare azoto (N2), preferibilmente una unità a membrana, ottenendo un gas di sintesi a ridotto contenuto di azoto e una corrente ricca di azoto; almeno una parte del gas di sintesi a ridotto contenuto di azoto (preferibilmente tutto) è utilizzata come combustibile; la restante parte è alimentata alla sintesi dell'ammoniaca insieme alla corrente ricca di azoto.

Questa configurazione è particolarmente vantaggiosa se l'aria arricchita in O2 non ha una purezza elevatissima (ad esempio inferiore a 95% di O2), e/o se il gas naturale contiene azoto. Si ottengono tre benefici: di aumentare il potere calorifico del fuel gas, di ridurre la portata di fumi di combustione (e la potenza del rispettivo ventilatore, ID fan), e di conservare l'azoto che è un reagente per l'ammoniaca. L'unità di separazione dell'azoto a membrana è ulteriormente preferita perché detta unità può operare sfruttando la differenza di pressione tra il gas di sintesi (prodotto a elevata pressione) e la combustione nel forno (che avviene a pressione atmosferica). Inoltre la corrente ricca di azoto, che va alla sintesi, non perde pressione.

La configurazione appena descritta, che prevede separazione dell'azoto dal gas di sintesi, è applicabile anche in un processo convenzionale, con steam reformer primario e reformer secondario ad aria, ottenendo il vantaggio di non dover modificare o ingrandire il compressore aria. Tuttavia con un secondario ad aria, e senza modificare il compressore e quindi non potendo aumentare la portata di aria, si dovrebbe produrre la quota aggiuntiva di gas di sintesi (richiesto come fuel) aumentando la capacità del reformer primario e/o installando un reformer riscaldato a gas (GHR), entrambe le soluzioni essendo molto costose. Per questi motivi la descritta separazione dell'azoto è particolarmente preferita in combinazione all'uso dell'aria arricchita nella fase di conversione del gas naturale in gas di sintesi.

In alcune realizzazioni, è prevista una espansione, con produzione di lavoro meccanico, del gas di sintesi a ridotto contenuto di CO2 dopo averlo opzionalmente scaldato. Detto gas è disponibile a una pressione maggiore della pressione richiesta per la combustione in forno, pertanto può essere espanso in una macchina adeguata, come un espansore o una turbina, producendo lavoro meccanico. Per esempio detta espansione può essere da circa 25 a circa 3 bar. Il gas ha un volume specifico elevato dato che comprende essenzialmente H_2, e per questo la sua espansione può generare una potenza ragguardevole. La potenza ottenuta può coprire in parte i fabbisogni del processo, rendendolo più efficiente.

In alcune realizzazioni la fase di shift comprende due fasi a diversa temperatura, per esempio preferibilmente uno shift ad alta temperatura (HTS) per esempio su catalizzatore a base Ferro seguito da uno shift a bassa temperatura (LTS) o a media temperatura (MTS) per esempio su catalizzatore a base Rame. Il vantaggio correlato è di ottenere la massima conversione del CO in CO2, che sarà poi separata nella fase di decarbonatazione, in modo da avere il minimo contenuto residuo di CO nel gas di sintesi utilizzato come combustibile. Dato che il CO è una fonte di CO2, durante la combustione, si ottiene il vantaggio di minimizzare le emissioni di CO2 a camino.

La conversione del gas naturale in gas di sintesi, ad esempio tramite reforming, avviene preferibilmente a pressione inferiore a 50 bar, più preferibilmente inferiore a 40 bar, più preferibilmente inferiore a 30 bar.

Generalmente l'arte nota insegna a privilegiare pressioni di conversione alte, per aumentare la capacità della sezione di conversione (front-end) e per ridurre il consumo della compressione del gas di sintesi. La presente invenzione invece è preferibilmente messa in opera con pressioni di conversione basse per ottenere la massima conversione del metano, perché la reazione di steam reforming è favorita a pressione inferiore, in modo da

avere il minimo contenuto residuo di metano nel gas di sintesi utilizzato come combustibile. Dato che il metano è una fonte di CO2, durante la combustione, si ottiene il vantaggio di minimizzare le emissioni di CO2 a camino.

In alcune realizzazioni il rapporto vapore/carbonio (steam to carbon, S/C) globale nella fase di conversione è maggiore di 2.0, preferibilmente maggiore di 2.4 e più preferibilmente maggiore di 2.7. Generalmente l'arte nota insegna a privilegiare S/C bassi per aumentare la capacità della sezione di conversione (front-end). L'invenzione in contrasto prevede un rapporto S/C relativamente alto per massimizzare la conversione del metano, e del CO nella fase di shift, e ridurre la concentrazione di CH4 e CO nel gas di sintesi. Dato che il metano e CO sono una fonte di CO2, durante la combustione, si ottiene il vantaggio di minimizzare le emissioni di CO2 a camino.

Il gas di sintesi a ridotto contenuto di CO2 preferibilmente costituisce tutto, o sostanzialmente tutto, il combustibile dei forni utilizzati per il processo. In alcune realizzazioni tuttavia si preferisce mantenere una piccola quantità di gas naturale che è denominata "trim fuel" del forno. Preferibilmente detta piccola quantità ha un contributo al calore di combustione totale del forno (duty) inferiore al 15%, più preferibilmente inferiore al 10%. Il trim fuel consente di controllare rapidamente il forno, per esempio per alzare o abbassare il carico velocemente in caso di necessità.

Detto contributo al calore di combustione è esprimibile come il prodotto tra portata (kg/s o mol/s) e potere calorifico (J/kg o J/mol).

L'invenzione ottiene emissioni di CO2 inferiori a 0.5 t/t (ton di CO2 emessa per ton di ammoniaca prodotta); in realizzazioni preferite dell'invenzione le emissioni sono inferiori a 0.3 t/t, o inferiori a 0.2 t/t.

Per quanto riguarda l'impianto, i forni sono vantaggiosamente equipaggiati con bruciatori "dual fuel", adatti a bruciare sia gas naturale sia il gas di sintesi.

L'invenzione può richiedere la installazione di una unità di separazione aria (ASU) per produrre l'aria arricchita, e opzionalmente azoto.

L'invenzione può essere applicata anche ai processi e impianti ammoniaca-urea. Un impianto ammoniaca-urea è un impianto comprendente una prima sezione di sintesi di ammoniaca e una seconda sezione di sintesi di urea da ammoniaca e CO2, in cui almeno una parte dell'ammoniaca prodotta nella prima sezione alimenta la seconda sezione. In questo caso anche la CO2 separata nella fase di decarbonatazione alimenta vantaggiosamente detta seconda sezione di sintesi di urea.

I principali vantaggi dell'invenzione sono i seguenti.

La separazione del CO2 avviene da un gas di sintesi che è concentrato in CO2 (15-25% mol) ed è a pressione relativamente alta, pertanto la separazione di CO2 è da questa corrente è molto più agevole e richiede meno consumo di energia rispetto a separate CO2 da fumi di combustione.

Il sistema dell'invenzione non richiede solvente per la cattura di CO2 da fumi.

L'uso di aria arricchita in ossigeno introduce diversi vantaggi:

- aumenta il potere calorifico del gas di sintesi;
- la combustione del gas di sintesi genera meno fumi rispetto alla combustione di gas naturale, a parità di calore rilasciato, perché la combustione di idrogeno (contenuto nel gas di sintesi) avviene con riduzione del numero di moli contrariamente alla combustione del metano, per cui la convettiva del reformer è più piccola e richiede un ventilatore (induced draft fan o ID fan) meno potente;

- limita la perdita a camino di azoto (che è un reagente), evitando uno spreco di energia di separazione e compressione di N2; la generazione di azoto per la sintesi non deve essere ingrandita;

- permette di tenere un'alta temperatura di conversione del gas naturale, libera dal vincolo di non introdurre azoto in eccesso rispetto alla stechiometria della sintesi NH3 (tipico dei processi convenzionali, ad aria) con un'elevata conversione del metano che rende minime le emissioni di CO2.

Negli impianti convenzionali con reformer secondario ad aria, l'aria di processo è alimentata a detto reformer secondario in quantità stechiometrica, cioè nella quantità richiesta per raggiungere un rapporto di H/N circa 3 nel make-up gas. Ciò significa che la portata di aria (in particolare la quantità di ossigeno introdotto nel reformer) non può essere scelta liberamente, ad esempio per raggiungere una conversione completa del NG.

Invece, se l'ossidante e l'azoto sono alimentati separatamente al processo, si può scegliere la portata di ossidante per ottenere una conversione completa del gas naturale ed eventualmente aggiungere a valle l'azoto che serve per la composizione di make-up gas desiderata. Il vantaggio della conversione completa è di produrre un gas di sintesi con minore contenuto di metano, e quindi minori emissioni di CO2.

Un altro vantaggio dell'invenzione è che la maggiore portata di gas nel frontend permette di recuperare più calore e di generare più vapore. La maggior quantità di vapore prodotto nel frontend limita il carico dei rispettivi apparecchi ausiliari di generazione del vapore; un vantaggio è che il consumo di combustibile (e potenziale sorgente di emissioni di CO2) è rappresentato sostanzialmente solo dal reformer primario o riscaldatore (o fired heater). Sostituendo il combustibile del reformer con gas di sintesi (e se necessario

sostituendo i relativi bruciatori) si ottiene un sostanziale abbattimento o annullamento delle emissioni di CO2.

Un altro vantaggio è che l'invenzione non richiede di separare idrogeno dal gas di sintesi a ridotto contenuto di CO2, cioè di purificare il gas di sintesi a ridotto contenuto di CO2 in un gas ricco in H2 ed un "waste gas". Il gas di sintesi a ridotto contenuto di CO2 si può usare direttamente per la sintesi di ammoniaca dopo eventuale metanazione.

Quando applicata all'ammodernamento (revamping) di impianti, l'invenzione ottiene notevoli sinergie che permettono di ridurre le emissioni di CO2 senza perdere produzione, limitando modifiche e costi. Questo perché l'invenzione:

- riduce molto la portata di gas nel frontend, e quindi le relative apparecchiature e tubazioni (secondario, shift, decarbonatazione metanazione) sono adatte per una capacità maggiore;
- detta capacità maggiore corrisponde al gas di sintesi da usare come fuel;
- può usare una temperatura alta di uscita dal secondario (ottenendo una conversione completa del metano), perché l'azoto si aggiunge separatamente dall'ossigeno; pertanto il metodo dell'invenzione produce il gas in più da usare come combustibile senza richiedere costose modifiche del reformer primario anche quando detto reformer è sostanzialmente al limite della capacità;
- sbottiglia la sezione di rimozione CO2, perché aumenta la pressione parziale di CO2 e riduce la portata di gas nell'assorbitore;
- la combustione del CO2-depleted syngas genera meno fumi del NG, per cui la convettiva del reformer e ventilatore (ID fan) sono scaricati;

- si deve modificare solo il frontend, mentre il backend (compressore del gas di sintesi, sintesi dell'ammoniaca, sezione frigorifera) è sostanzialmente inalterato.

- il processo non necessita di una purificazione spinta del gas di sintesi per rimuovere gli inerti, essendo sufficiente usare il metanatore (spesso esistente); in particolare, non è necessario alcuno step di separazione del gas di sintesi in una corrente di H2 e gas di scarto (waste gas).

Descrizione delle figure

La Fig. 1 illustra una prima realizzazione dell'invenzione.

La Fig. 2 illustra una seconda realizzazione.

Descrizione di modi preferiti di realizzare l'invenzione

La FIG 1 mostra un processo secondo un modo di realizzare l'invenzione basato su pre-reformer e reformer autotermico ATR ad ossigeno.

I blocchi di Fig. 1 denotano i seguenti sistemi o apparecchi:

AUX	forno preriscaldatore della carica e caldaia ausiliaria (auxiliary boiler)
PRE	pre-reformer
ATR	reformer autotermico
SHF	sezione di shift
CDR	sezione di rimozione CO2 (decarbonatazione)
MET	metanatore
SYN	sezione di sintesi
HRU	sezione di recupero idrogeno

ASU sezione di separazione (frazionamento) aria

Una carica 10 comprendente gas naturale e vapore è preriscaldata in AUX e convertita in un gas di sintesi 11 attraverso i reformer PRE e ATR. Il reformer autotermico ATR opera con una corrente 22 di aria arricchita o di ossigeno.

Il gas di sintesi 11, contenente H2, CO e CO2, è sottoposto a reazione di shift in SHF e successivamente a rimozione di CO2 in CDR. La sezione SHF può comprendere trattamenti di shift a diversa temperatura. La sezione CDR per esempio opera con lavaggio chimico-fisico del gas con soluzione acquosa di ammine.

La sezione CDR produce un gas di sintesi 12 a ridotto contenuto di CO2 e una corrente 13 di CO2 che può essere sequestrata o utilizzata per altri scopi di processo, ad esempio per produrre urea.

Preferibilmente il gas di sintesi 12 ha la seguente composizione: 98% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

Una parte 14 di gas a ridotto contenuto di CO2 è utilizzata come combustibile in un forno nel front-end, per esempio in un riscaldatore della carica (blocco AUX). La restante parte 18 di gas di sintesi è ulteriormente trattata nel metanatore MET.

Nell'esempio la quota fuel 14 di gas di sintesi, insieme a un gas di coda 15 della sezione HRU, alimenta uno o più utilizzatori del blocco AUX attraverso la linea fuel 16. Opzionalmente una quantità opportuna di gas naturale 17 (trim fuel) è aggiunta al gas 16.

La quota processo 18 del gas di sintesi, dopo passaggio nel metanatore (opzionale), è addizionata con azoto 19 proveniente dalla sezione di separazione aria ASU.

Il gas così ottenuto, insieme a una corrente di idrogeno 20 recuperata dalla sezione HRU, alimenta la sezione di sintesi SYN. Detta sezione di sintesi produce ammoniaca 23 e una corrente 21 di gas di spurgo trattato nella sezione HRU per il recupero dell'idrogeno in essa contenuto.

La sezione di separazione ASU produce, oltre all'azoto 19, anche la corrente 22 di aria arricchita o di ossigeno per il reformer autotermico ATR.

La FIG 2 mostra un processo secondo un modo preferito di realizzare l'invenzione basato su reforming primario e ATR.

Il blocco SMR di Fig. 1 denota il reformer primario più ausiliari, ad es. generatori di vapore. I restanti simboli di Fig. 2 corrispondono ai simboli di Fig. 1 e pertanto la descrizione non è ripetuta.

In Fig. 2 è mostrata anche una linea opzionale 15a per riciclare parte del gas di coda 15 dalla unità HRU all'alimentazione del reformer primario SMR.

Il processo di Fig. 1 o Fig. 2 consente di produrre ammoniaca con emissioni di circa 0.1 t/t contro circa 0.7 t/t dell'arte nota.

Lo schema di Fig. 2 in una realizzazione preferita è il risultato dell'ammodernamento di un impianto ammoniaca con reformer secondario ad aria.

In una realizzazione, la procedura di ammodernamento comprende essenzialmente i seguenti passi:

installare l'unità ASU per generare la corrente 22 di ossigeno o aria arricchita;

modificare il reformer secondario per accettare detta corrente 22 invece di aria;

aumentare la quota di gas naturale destinato al processo e ridurre la quota di gas naturale destinato a fuel;

rivampare la esistente sezione di desolforazione del gas naturale per aumentarne la capacità in ragione della maggiore portata di gas di processo;

rivampare la esistente sezione CDR per aumentarne la capcità in ragione della maggiore quantità di CO2 da separare.

Si comprende che l'ammodernamento non richiede di fare costose modifiche al reformer, agli scambiatori e tubazioni del frontend, alla sezione di shift. Ciò è dovuto al fatto che la portata volumetrica di gas attraverso il front-end non aumenta nonostante la generazione della quota aggiuntiva di gas (quota fuel).

Esempio

La tabella 1 seguente si riferisce a un impianto con capacità di 3000 ton metriche per giorno (MTD) di ammoniaca prodotta.

La tabella 1 confronta le seguenti opzioni:

(1): impianto dell'arte nota con reformer primario e reformer secondario alimentato ad aria.

(2): impianto dell'arte nota, come da opzione (1), con cattura del CO2 dai fumi del reformer primario.

(3): impianto secondo l'invenzione, come da Fig. 1.

(4): impianto secondo l'invenzione, come da Fig. 2.

Tabella 1

		(1) Arte nota	(2) Arte nota	(3) Inv.	(4) Inv.
Produzione di ammoniaca	MTD	3000	3000	3000	3000
Consumo netto di gas naturale per ton di ammoniaca (feed+fuel-vapore esportato e.g. verso sezione urea)	Gcal/ton	6.7	7.4	7.0	6.9
Differenza rispetto (1)	Gcal/ton		+0.7	+0.3	+0.2
CO2 catturato nel processo	MTD	3600	3600	5200	5100
CO2 in atmosfera (contenuto nei fumi)	MTD	2100	200	200	200
CO2 in atmosfera (contenuto nei fumi)	t/t	0.7	0.1	0.1	0.1
Taglia degli apparecchi					
Forni (reformer/forni + caldaie ausiliarie)	%	100	120	75	105
Capacità di rimozione CO2	%	100	100	145	140
Capacità ossigeno da ASU	%	n/a	n/a	100	60
Portata del frontend (uscita secondario / ATR)	%	100	100	120	97

(*) il consumo netto è espresso in Gcal/t riferite al potere calorifico inferiore (LHV) del gas naturale.

La tabella mostra che il processo dell'invenzione (opzione 3) richiede un front-end adeguato per produrre anche la quota di gas da usare come combustibile nei forni, infatti la quantità di CO2 catturata nel processo ammonta a 5200 MTD rispetto a 3600 delle opzioni (1) e (2), e la portata di gas di sintesi nel frontend è circa il 20% in più. Nonostante questo il consumo dell'impianto è inferiore al consumo della opzione (2) essendo pari a 7.0 invece di 7.4 Gcal/ton; il consumo è competitivo con l'impianto senza cattura secondo l'opzione (1). Il carico (duty) totale dei forni è solo il 75% del caso (1).

Nel caso (4) il consumo energetico ottenuto è inferiore al caso (3), pari a 6.9 Gcal/ton, e anche il costo dell'impianto è inferiore. Questo perché nel caso (4) la quantità di CO2 separata nel processo è inferiore rispetto a (3); il duty dei forni è maggiore rispetto a (3) ma è confrontabile con le opzioni (1) e (2); il consumo di ossigeno è nettamente inferiore a (3); la portata nel frontend è nettamente inferiore a (3) e sostanzialmente pari a (1) e (2).

Gli esempi mostrano come il nuovo processo sia più efficiente e competitivo dell'arte nota.

L'esempio mostra anche il vantaggio di rivampare un impianto operante come da opzione (1), preferibilmente implementando l'opzione (4). Infatti, in questa ipotesi il duty dei forni e la portata di gas restano sostanzialmente immutate mentre si abbattono le emissioni di CO2. L'invenzione così raggiunge lo scopo di minimizzare le emissioni di CO2 di un impianto convenzionale senza perdere produzione di ammoniaca.

RIVENDICAZIONI

1) Processo di sintesi dell'ammoniaca da gas naturale comprendente:

conversione di una carica di gas naturale desolforato e vapore, con aria arricchita in ossigeno o con ossigeno, in un gas di sintesi (11) contenente idrogeno, CO e CO2, all'interno di una sezione di conversione,

un trattamento di detto gas di sintesi (11) comprendente almeno una reazione di shift del monossido di carbonio in CO2, e successiva separazione di CO2 dal gas, così ottenendo un gas di sintesi (12) a ridotto contenuto di CO2 e una corrente gassosa ricca di CO2, contenente il CO2 separato dal gas;

opzionalmente, una fase di metanazione del gas di sintesi e/o una aggiunta di azoto al gas di sintesi,

caratterizzato dal fatto che

una parte (14) di detto gas di sintesi (12) a ridotto contenuto di CO2 è separata come quota combustibile, e detta quota combustibile (14) è alimentata come combustibile a almeno un forno .

2) Processo secondo la rivendicazione 1, in cui detta quota combustibile (14) è compresa tra 1% e 40% della quantità totale di detto gas di sintesi (12) a ridotto contenuto di CO2, preferibilmente tra 10% e 30%.

3) Processo secondo la rivendicazione 1 o 2, in cui detta quota combustibile è separata a monte della fase di metanazione o a monte della fase di aggiunta di azoto.

4) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detto gas di sintesi (12) a ridotto contenuto di CO2 contiene non più di 1000 ppm in volume di CO2.

5) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detta aria arricchita contiene almeno il 50% di ossigeno, preferibilmente almeno il 90%.

6) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detta quota combustibile (14) del gas di sintesi alimenta uno o più tra i seguenti apparecchi: un forno per la produzione e/o surriscaldo di vapore; uno o più bruciatori di un reformer primario a vapore; uno o più forni di pre-riscaldo della carica di un reformer autotermico o di un reattore a ossidazione parziale o di una sezione di desolforazione del gas naturale.

7) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui: un gas di spurgo (21) del processo di sintesi dell'ammoniaca, contenente idrogeno e metano, è trattato per recuperare l'idrogeno in esso contenuto, con ottenimento di un gas ricco di idrogeno (20) e di un gas di coda (15) contenente metano; almeno parte (15a) di detto gas di coda (15) è riciclata come gas di processo e sottoposta alla detta fase di conversione del gas naturale in gas di sintesi.

8) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui: una parte del detto gas di sintesi (12) a ridotto contenuto di CO2 è trattata in un'unità per separare azoto ottenendo una prima corrente di gas di sintesi a ridotto contenuto di azoto e una seconda corrente ricca di azoto; almeno una parte di detta prima corrente, preferibilmente tutta, è utilizzata come combustibile; la eventuale restante parte di detta prima corrente è alimentata alla sintesi dell'ammoniaca insieme alla seconda corrente.

9) Processo secondo una qualsiasi delle rivendicazioni precedenti comprendente anche una fase di espansione, con produzione di lavoro meccanico, del gas di sintesi (12) a ridotto contenuto di CO2, opzionalmente dopo averlo scaldato.

10) Processo secondo una qualsiasi delle rivendicazioni precedenti in cui il rapporto vapore/carbonio globale nella fase di conversione è maggiore di 2.0, preferibilmente maggiore di 2.4 e più preferibilmente maggiore di 2.7.

11) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui:

detta quota fuel (14) di gas di sintesi costituisce tutto il combustibile dei forni utilizzati nella sezione di conversione, o

è presente una quantità di gas naturale come combustibile di regolazione (trim fuel), il contributo di detto combustibile di regolazione al calore di combustione totale essendo non superiore al 15%.

12) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui le emissioni di CO2 sono inferiori a 0.5 ton di CO2 emessa per ton di ammoniaca prodotta.

13) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui la conversione del gas naturale in gas di sintesi comprende: un reforming primario del gas naturale in presenza di vapore e un reforming secondario effettuato con detta corrente di ossigeno o aria arricchita.

14) Metodo di ammodernamento di un impianto per la sintesi dell'ammoniaca da gas naturale o impianto ammoniaca-urea, in cui:

l'impianto comprende una sezione di reforming che include un reformer primario con vapore e reformer secondario ad aria, e una sezione di trattamento del gas di sintesi tramite shift di monossido di carbonio in diossido di carbonio, decarbonatazione e eventualmente metanazione,

e il metodo di ammodernamento comprende almeno:

fornire una corrente (22) di aria arricchita o di ossigeno e utilizzare detta corrente quale ossidante, al posto dell'aria, per il reformer secondario;

separare una quota parte (14) del gas di sintesi, a valle della decarbonatazione, per utilizzo come quota combustibile, e destinare una restante quota di processo del gas di sintesi alla conversione in ammoniaca.

alimentare detta quota combustibile (14) del gas, avente un ridotto contenuto di CO2, come combustibile per almeno un forno dell'impianto.

15) Metodo di ammodernamento secondo la rivendicazione 14 comprendente: installare una unità di separazione aria per fornire detta corrente di aria arricchita o di ossigeno, in cui detta unità di separazione fronisce anche una corrente di azoto che viene aggiunta alla quota di processo del gas di sintesi per ottenere il desiderato rapporto tra H2 e N2.

RIASSUNTO

Processo di sintesi dell'ammoniaca da gas naturale comprendente conversione di una carica di gas naturale desolforato e vapore, con aria arricchita in ossigeno o con ossigeno, in un gas di sintesi (11), e trattamento del gas di sintesi (11) con shift e decarbonatazione, in cui una parte del gas di sintesi a ridotto contenuto di CO2, ottenuto dopo decarbonatazione, è separata e utilizzata come quota combustibile per uno o più forni della sezione di conversione, e la restante parte del gas è utilizzata per produrre ammoniaca.

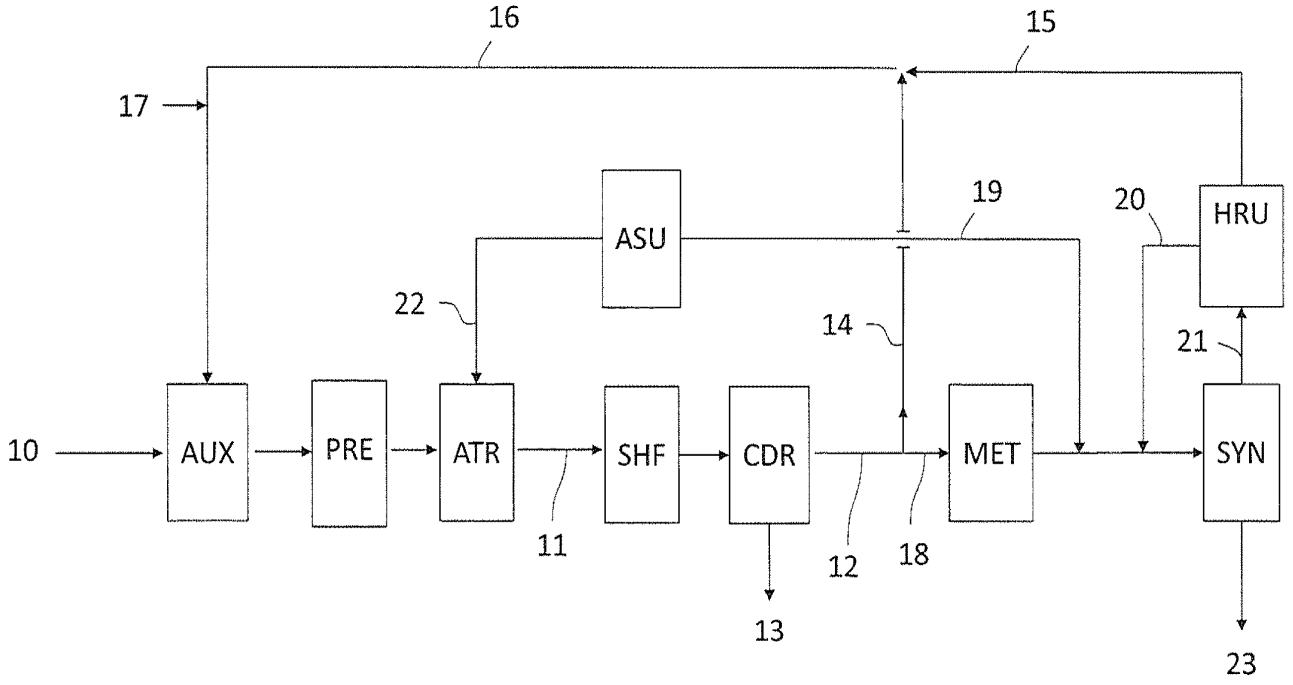

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FIG. 1

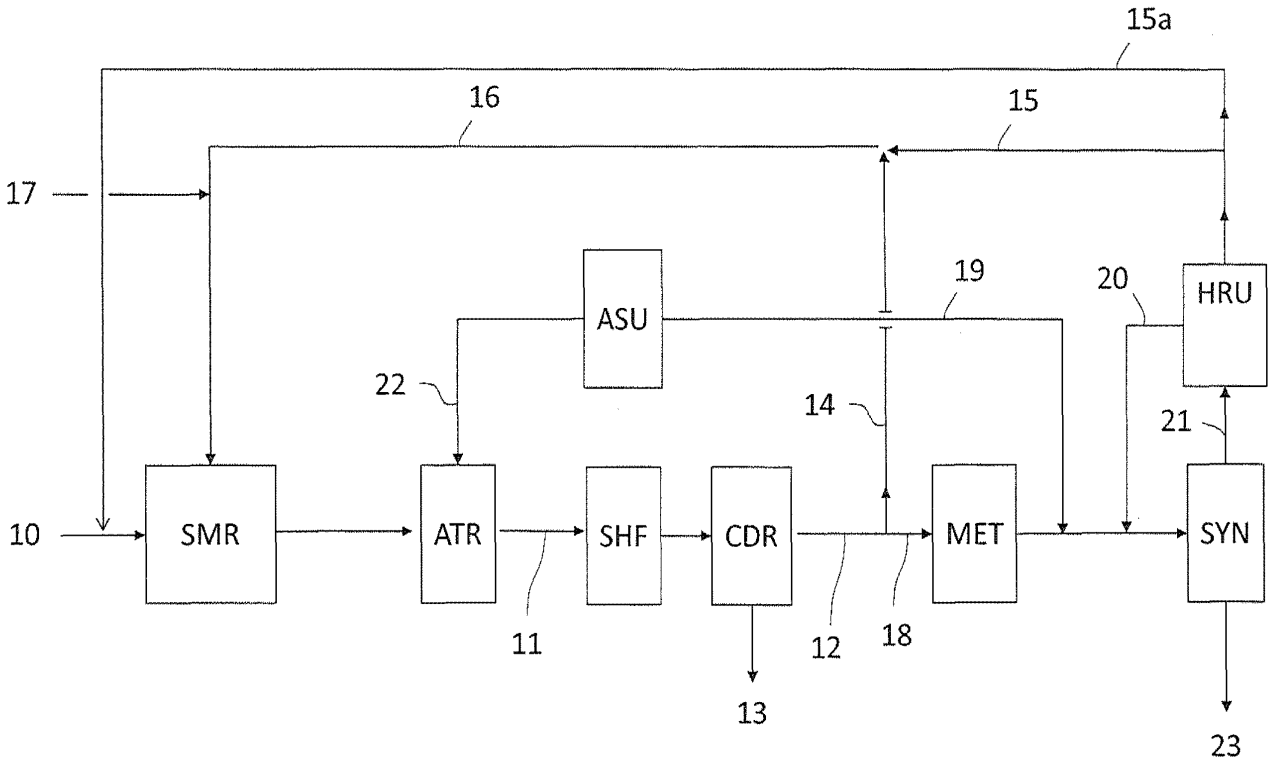

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FIG. 2

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DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:		**PCT/EP2018/052358**
International filing date:		**31 January 2018 (31.01.2018)**
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Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-*bis*)

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCHING AUTHORITY

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PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2018/052358	31.01.2018	15.02.2017

International Patent Classification (IPC) or both national classification and IPC
INV. C01B3/02 C01B3/36 C01C1/04

Applicant
CASALE SA

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	see form PCT/ISA/210	Werner, Håkan Telephone No. +49 89 2399-0

Form PCT/ISA/237 (Cover Sheet) (January 2015)

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed:

      ☐ in the form of an Annex C/ST.25 text file.

      ☐ on paper or in the form of an image file.

   b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

   c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

      ☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

      ☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2-4, 8, 9, 11-14
	No:	Claims	1, 5-7, 10, 15-18
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-18
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations

see separate sheet

SECTION V

1 Reference is made to the following documents:

D1 US 2004/234426 A1 (REDDY SATISH [US] ET AL) 25 November 2004 (2004-11-25)

D2 WO 2010/018550 A1 (AIR LIQUIDE [FR]; VAKIL TARUN D [US]; WOLF ULRICH [DE]) 18 February 2010 (2010-02-18)

D3 US 2015/031916 A1 (KISS GUENTER HANS [CH]) 29 January 2015 (2015-01-29)

D4 US 2014/248205 A1 (ALLAM RODNEY J [GB]) 4 September 2014 (2014-09-04)

2 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1, 5-7, 10 and 16-18 is not new in the sense of Article 33(2) PCT.

3 D1 discloses (in particular paragraphs [0023]-[0027], [0031], [0032] and [0034] and Figs. 2 and 3) a method for making ammonia comprising reforming natural gas using a gas comprising 90% oxygen from an ASU. The syngas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a coldbox whereby two streams are obtained. One stream is sent to the ammonia converter and the other stream is used as fuel in the primary reformer. Before the CO_2 depleted syngas is treated in a coldbox it is treated in a methanator. Therefore, the depleted syngas will inevitably have an amount of $CO_2 < 1000$ppm. The tail gas (=CO_2 depleted syngas used as fuel gas) can be compressed followed by expansion (paragraph [0031]). D1 further disclosed that existing ammonia plants can be revamped using the means disclosed in D1, namely an ASU and a coldbox with which two streams are obtained, one which is sent to the ammonia converter and the other which is used as fuel in the primary reformer.

Therefore, the subject-matter of claims 1, 5-7, 10 and 16-18 is not new vis-a-vis D1.

4 Note that the feature "the CO_2 emissions are less than 0.5 tonne of CO_2 emitted per tonne of ammonia produced" merely defines the result to be achieved and not the technical features for obtaining such result. Therefore, claim 16 lacks clarity (Art. 6 PCT).

Further note that using desulphurized natural gas for obtaining a synthesis gas is common practice. It can therefore be assumed that the natural gases used in the documents cited in this examining report are, at least to some extent, desulfurized.

5 Furthermore, the present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-18 does not involve an inventive step in the sense of Article 33(3) PCT.

6 D3, which can be considered to represent the most relevant state of the art, discloses (in particular: paragraphs [0012]-[0020] and Fig. 1) a method for making ammonia and urea with reduced CO_2 emission. A synthesis gas is produced using oxygen from an ASU. CO in the obtained syngas is converted into CO_2. Then CO_2 is removed from the syngas with now comprises H_2. The CO_2 depleted synthesis gas is combined with N_2 from the ASU whereby ammonia is obtained. Ammonia is reacted with CO_2 whereby urea is produced. The subject-matter of claims 1 and 14 therefore differs from this known method in that a part of the CO_2 depleted syngas is used as fuel.

7 The problem to be solved by the present invention may therefore be regarded as a method for making ammonia with further reduced CO_2 emission.

8 D2 discloses (in particular: page 3, line 23 - page 4, line 19; page 11, line 20 - page 12, line 8; page 17, lines 15-27; claim 7 and Figs. 2 and 3) a method for making syngas. Natural gas is reformed whereby a synthesis gas is obtained. The synthesis gas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a PSA unit where a H2 rich stream and a residual stream are obtained. The residual stream comprising H2 is used as fuel in the primary reformer. With this method enhanced CO_2 recovery during steam reforming can be obtained. Therefore, the person skilled in the art posed with the problem of further reducing CO_2 emission during ammonia production would take the teaching in D2 into account.

9 Furthermore, D4 discloses (in particular: paragraphs [0021], [0022] and [0034]-[0038] and Fig. 2) a process for producing ammonia syngas comprising converting natural gas, steam and oxygen enriched air into a syngas. The syngas (147) is splitted in an adsorber (155) into ammonia syngas (151) and a waste stram (152). The waste gas (152, 161, 182, 174) is used as fuel in a fired heater (103). The conversion of natural gas into syngas

includes converting on a partial oxidation reactor or in an autothermal reactor. Therefore, the person skilled in the art knows about using partial oxidation reactors and autothermal reactors during production of ammonia syngas.

10 Adapting the method disclosed in D3 by using some of the CO_2 depleted syngas as fuel for the primary reformer as disclosed in D2 hence renders the subject-matter of claims 1 and 17 obvious (Article 56 EPC).

11 Dependent claims 2-16 and 18 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT with respect to inventive step because the additional features of claims 2-16 and 18 do not seem to represent anything unusual for the person skilled in the art since these additional features are either disclosed in any of D2-D4 or represents obvious features for the person skilled in the art posed with the problem of optimising ammonia plants. Furthermore, these additional features do not seem be associated with any special technical effect that would justify inventiveness.

PCT REQUEST

Print Out (Original in Electronic Form)

0	**For receiving Office use only**	
0-1	International Application No.	**PCT/EP2018/052358**
0-2	International Filing Date	**31 JAN 2018 (31.01.2018)**
0-3	Name of receiving Office and "PCT International Application"	**RO/EP**

0-4	**Form PCT/RO/101 PCT Request**	
0-4-1	Prepared Using	PCT Online Filing Version 3.5.000.251e MT/FOP 20141031/0.20.5.20
0-5	**Petition** The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	**Receiving Office (specified by the applicant)**	European Patent Office (EPO) (RO/EP)
0-7	**Applicant's or agent's file reference**	AMC121BWO
I	**Title of Invention**	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE
II	**Applicant**	
II-1	This person is	Applicant only
II-2	Applicant for	All designated States
II-4	Name	CASALE SA
II-5	Address	Via Pocobelli 6 6900 Lugano Switzerland
II-6	State of nationality	CH
II-7	State of residence	CH
III-1	**Applicant and/or inventor**	
III-1-1	This person is	Inventor only
III-1-3	Inventor for	All designated States
III-1-4	Name (LAST, First)	BARATTO, Francesco
III-1-5	Address	Via Borgo Vico, 127 22100 Como Italy
III-2	**Applicant and/or inventor**	
III-2-1	This person is	Inventor only
III-2-3	Inventor for	All designated States
III-2-4	Name (LAST, First)	OSTUNI, Raffaele
III-2-5	Address	Via Montarina 21 6900 Lugano Switzerland

PCT REQUEST

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IV-1	**Agent or common representative; or address for correspondence**	
	The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	Agent
IV-1-1	Name (LAST, First)	ZARDI, Marco
IV-1-2	Address	c/o M. ZARDI & Co SA, Via Pioda, 6 6900 Lugano Switzerland
IV-1-3	Telephone No.	+41 91 910 65 00
IV-1-4	Facsimile No.	+41 91 910 65 09
V	**DESIGNATIONS**	
V-1	**The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.**	
VI-1	**Priority claim of earlier regional application**	
VI-1-1	Filing date	15 February 2017 (15.02.2017)
VI-1-2	Number	17156256.4
VI-1-3	Regional Office	EP
VI-2	**Priority claim of earlier regional application**	
VI-2-1	Filing date	06 October 2017 (06.10.2017)
VI-2-2	Number	17195305.2
VI-2-3	Regional Office	EP
VI-3	**Priority document request**	
	The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1 VI-2
VI-4	**Incorporation by reference :**	
	where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.	
VII-1	**International Searching Authority Chosen**	European Patent Office (EPO) (ISA/EP)

PCT REQUEST

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VII-2	**Request to use results of earlier search; reference to that search**	
VII-2-1	Filing date	15 February 2017 (15.02.2017)
VII-2-2	Application Number	17156256.4
VII-2-3	Country (or regional Office)	EP
VII-2-4	Statement (Rule 4.12(ii)):	This international application is the same, or substantially the same, as the application in respect of which the earlier search was carried out except, where applicable, that it is filed in a different language.
VII-2-5	Documents are available to the ISA in a form and manner acceptable to it and therefore do not need to be submitted by the applicant to the ISA (Rule 12bis.1(f)):	A copy of the results of the earlier search A copy of the earlier application A translation of the earlier application into a language which is accepted by the ISA
VII-3	**Request to use results of earlier search; reference to that search**	
VII-3-1	Filing date	06 October 2017 (06.10.2017)
VII-3-2	Application Number	17195305.2
VII-3-3	Country (or regional Office)	EP
VII-3-4	Statement (Rule 4.12(ii)):	This international application is the same, or substantially the same, as the application in respect of which the earlier search was carried out except, where applicable, that it is filed in a different language.
VII-3-5	Documents are available to the ISA in a form and manner acceptable to it and therefore do not need to be submitted by the applicant to the ISA (Rule 12bis.1(f)):	A copy of the results of the earlier search A copy of the earlier application A translation of the earlier application into a language which is accepted by the ISA

PCT REQUEST

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VIII	**Declarations**	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	–	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	–	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	–	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	–	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	–	
IX	**Check list**	Number of sheets	Electronic file(s) attached
IX-1	Request (including declaration sheets)	5	✓
IX-2	Description	32	✓
IX-3	Claims	4	✓
IX-4	Abstract	1	✓
IX-5	Drawings	4	✓
IX-7	TOTAL	46	
	Accompanying Items	Paper document(s) attached	Electronic file(s) attached
IX-8	Fee calculation sheet	–	✓
IX-19	Other	Pre-conversion archive	✓
IX-20	**Figure of the drawings which should accompany the abstract**	1	
IX-21	**Language of filing of the international application**	English	
X-1	**Signature of applicant, agent or common representative**	(PKCS7 Digital Signature)	
X-1-1	Name (LAST, First)	ZARDI, Marco	
X-1-3	Capacity (if such capacity is not obvious from reading the request)	(Representative)	

PCT REQUEST

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FOR RECEIVING OFFICE USE ONLY

10-1	**Date of actual receipt of the purported international application**	**31 JAN 2018 (31.01.2018)**
10-2	**Drawings:**	received
10-2-1	Received	
10-2-2	Not received	
10-3	**Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application**	
10-4	**Date of timely receipt of the required corrections under PCT Article 11(2)**	
10-5	**International Searching Authority**	**ISA/EP**
10-6	**Transmittal of search copy delayed until search fee is paid**	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	**Date of receipt of the record copy by the International Bureau**	

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(30) Priority Data:
17156256.4 15 February 2017 (15.02.2017) EP
17195305.2 06 October 2017 (06.10.2017) EP

(71) Applicant: **CASALE SA** [CH/CH]; Via Pocobelli 6, 6900 Lugano (CH).

(72) Inventors: **BARATTO, Francesco**; Viale Varese 83, 22100 Como (IT). **OSTUNI, Raffaele**; Via Montarina 21, 6900 Lugano (CH).

(74) Agent: **ZARDI, Marco**; c/o M. ZARDI & Co SA, Via Pioda, 6, 6900 Lugano (CH).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

WO 2018/149641 A1

(54) Title: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

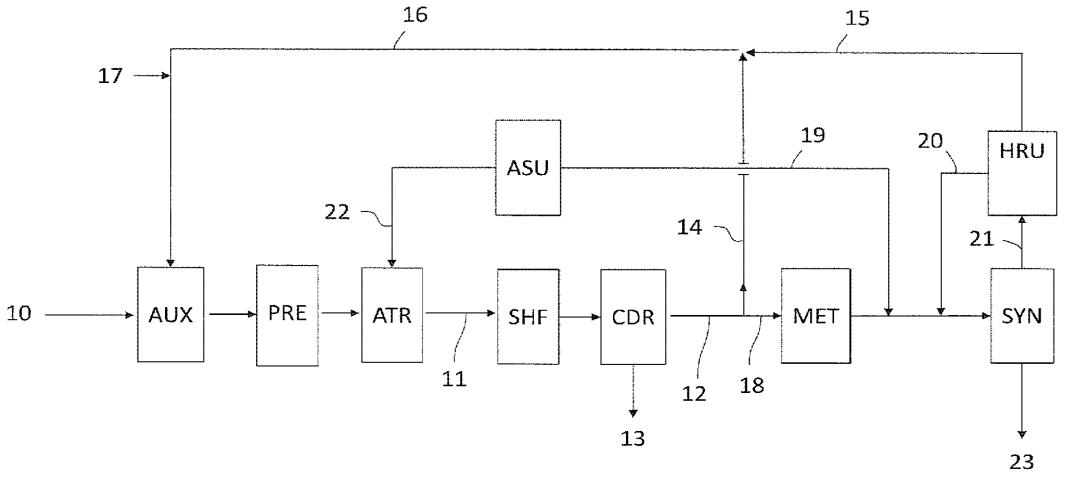


FIG. 1

(57) Abstract: Process for the synthesis of ammonia from natural gas comprising conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or oxygen, into a synthesis gas (11), and treatment of the synthesis gas (11) with shift reaction and decarbonation, wherein a part of the CO2-depleted synthesis gas, obtained after decarbonation, is separated and used as fuel fraction for one or more furnaces of the conversion section, and the remaining part of the gas is used to produce ammonia.

[Continued on next page]

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

CLAIMS

1) Process for synthesis of ammonia from natural gas, comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas (11) containing hydrogen, CO and CO2, in a conversion section;

a treatment of said synthesis gas (11) comprising at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas (12) and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas,

characterized by:

separation of a part (14) of said CO2-depleted synthesis gas (12) as fuel fraction, wherein said fuel fraction (14) is fed as fuel to at least one furnace.

2) Process according to claim 1, wherein said separation of the fuel fraction comprises the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia, optionally after further purification.

3) Process according to claim 1 or 2, wherein said fuel fraction (14) is comprised between 1% and 40% of the total amount of said CO2-depleted syngas (12), preferably between 10% and 30%.

4) Process according to any one of the preceding claims, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

5) Process according to any one of the preceding claims, wherein said CO2-depleted syngas (12) contains no more than 1000 ppm by volume of CO2.

6) Process according to any one of the preceding claims, wherein said enriched air contains at least 50% of oxygen, preferably at least 90% oxygen.

7) Process according to any one of the preceding claims, wherein said fuel fraction (14) of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

8) Process according to any one of the preceding claims, wherein: a purge gas (21) of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in it, obtaining a hydrogen-rich gas (20) and a tail gas (15) containing methane; at least part (15a) of said tail gas (15) is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

9) Process according to any one of the preceding claims, wherein: a part of said CO2-depleted syngas (12) is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, preferably all of it, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

10) Process according to any one of the preceding claims, also comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas (12), optionally after heating it.

11) Process according to any one of the preceding claims, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0, preferably

greater than 2.4 and more preferably greater than 2.7.

12) Process according to any one of the preceding claims, wherein

said synthesis gas fuel fraction (14) forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

13) Process according to any one of the preceding claims, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

14) Process according to any one of the preceding claims, wherein:

the conversion of the natural gas charge into synthesis gas comprises a step of autothermal reforming, optionally with pre-reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

15) Process according to any one of the preceding claims, wherein the conversion of the natural gas into synthesis gas comprises: primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

16) Process according to any one of the preceding claims, wherein the CO2 emissions are less than 0.5 tonnes of CO2 emitted per tonne of ammonia

produced.

17) Method for revamping a plant for the synthesis of ammonia from natural gas or ammonia/urea plant, wherein

the plant comprises a reforming section which includes a primary steam reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by means of a shift reaction of carbon monoxide into carbon dioxide, decarbonation and optionally methanation.

and the revamping method comprises at least:

providing a flow (22) of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part (14) of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction (14) of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

18) Method for revamping according to claim 17 comprising: installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

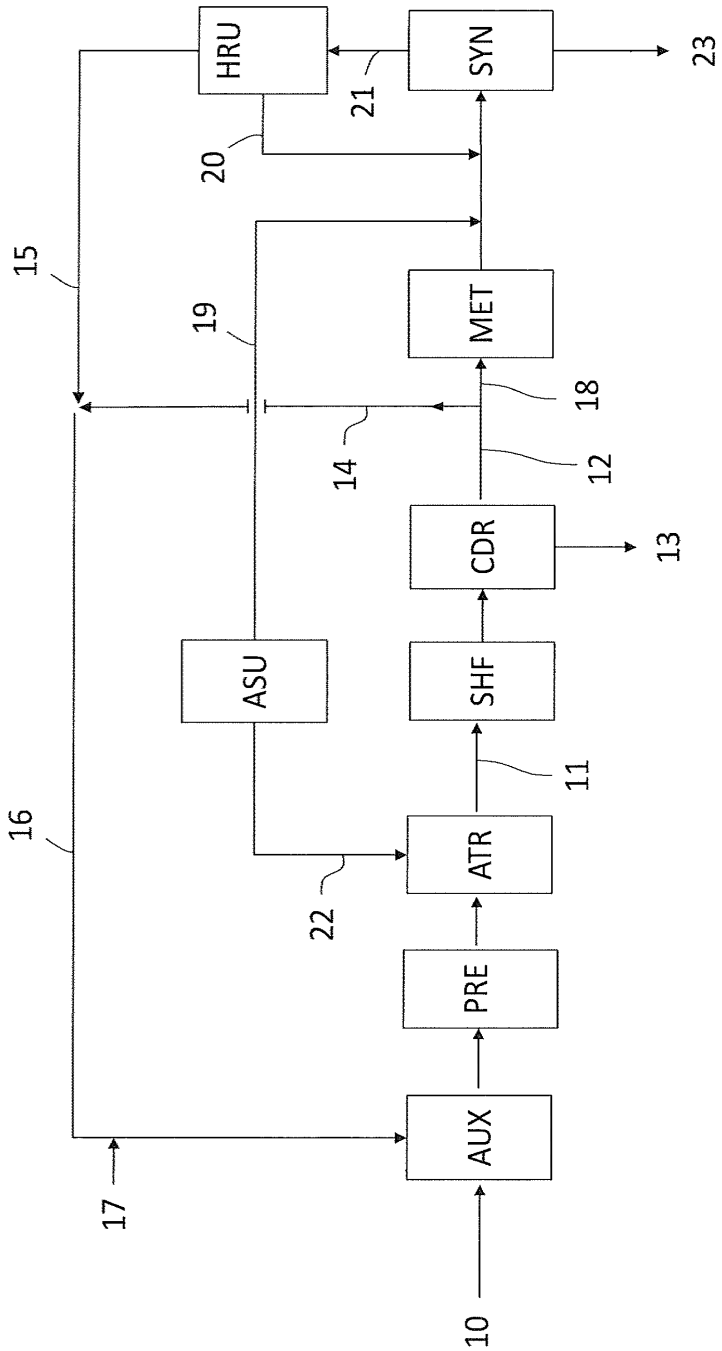

HRU
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ATR
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FIG. 1

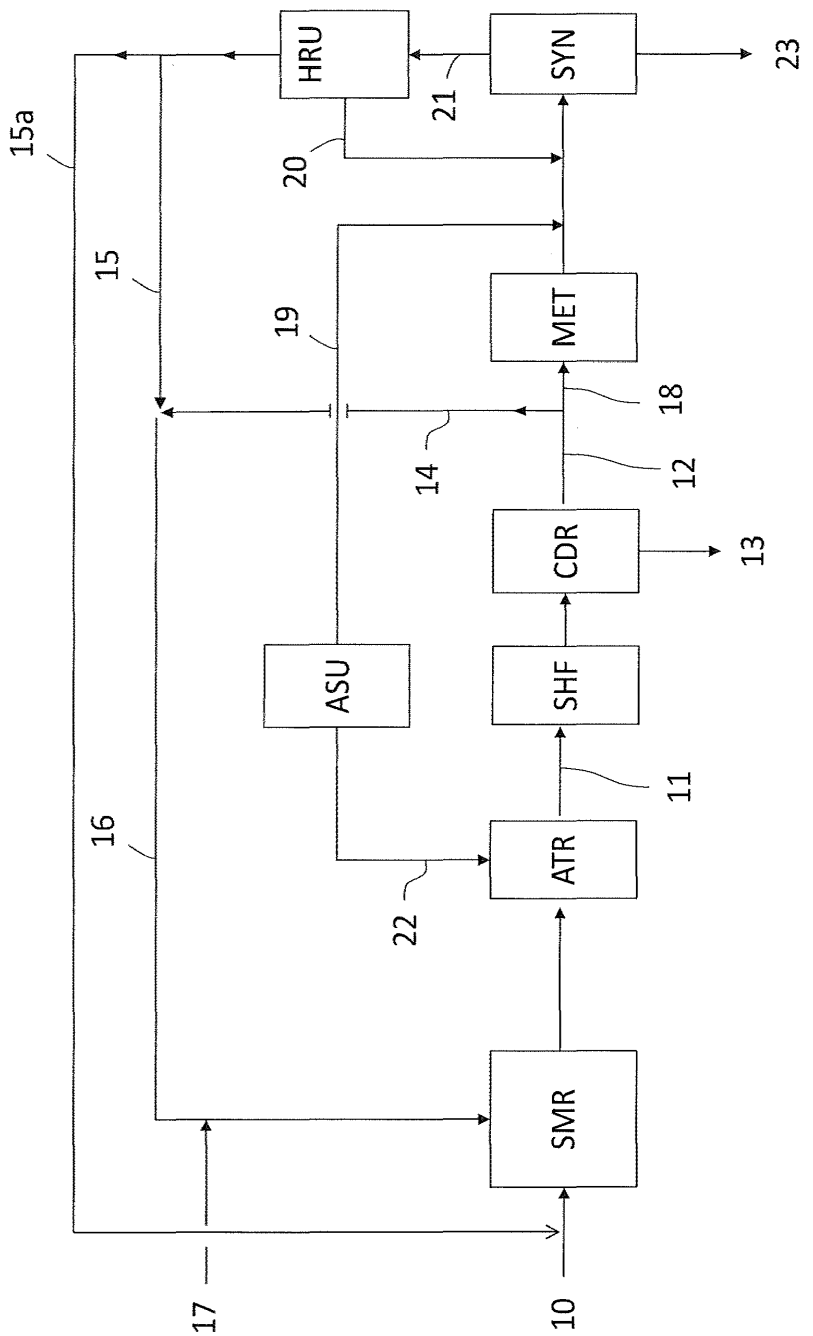

HRU
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FIG. 2

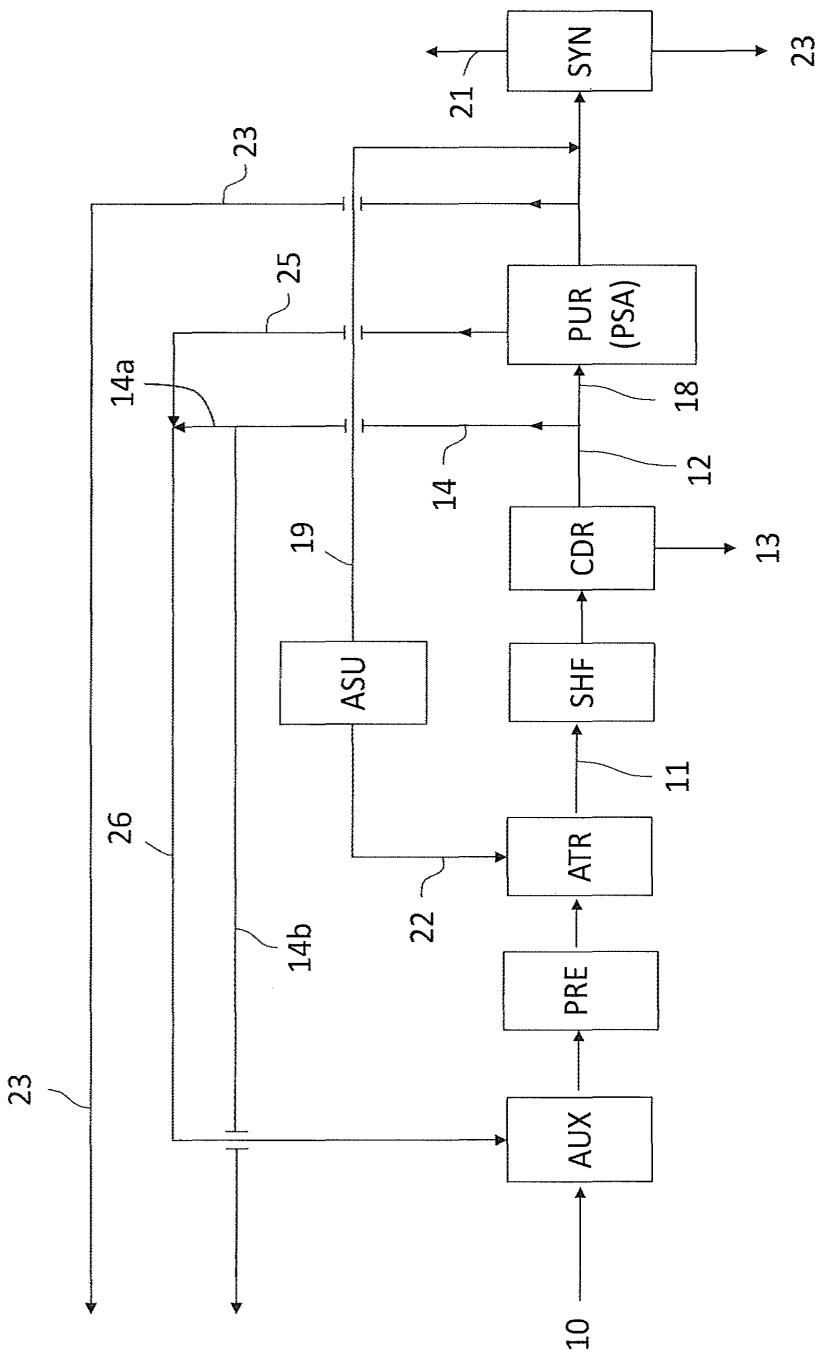

SYN
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AUX
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FIG. 3

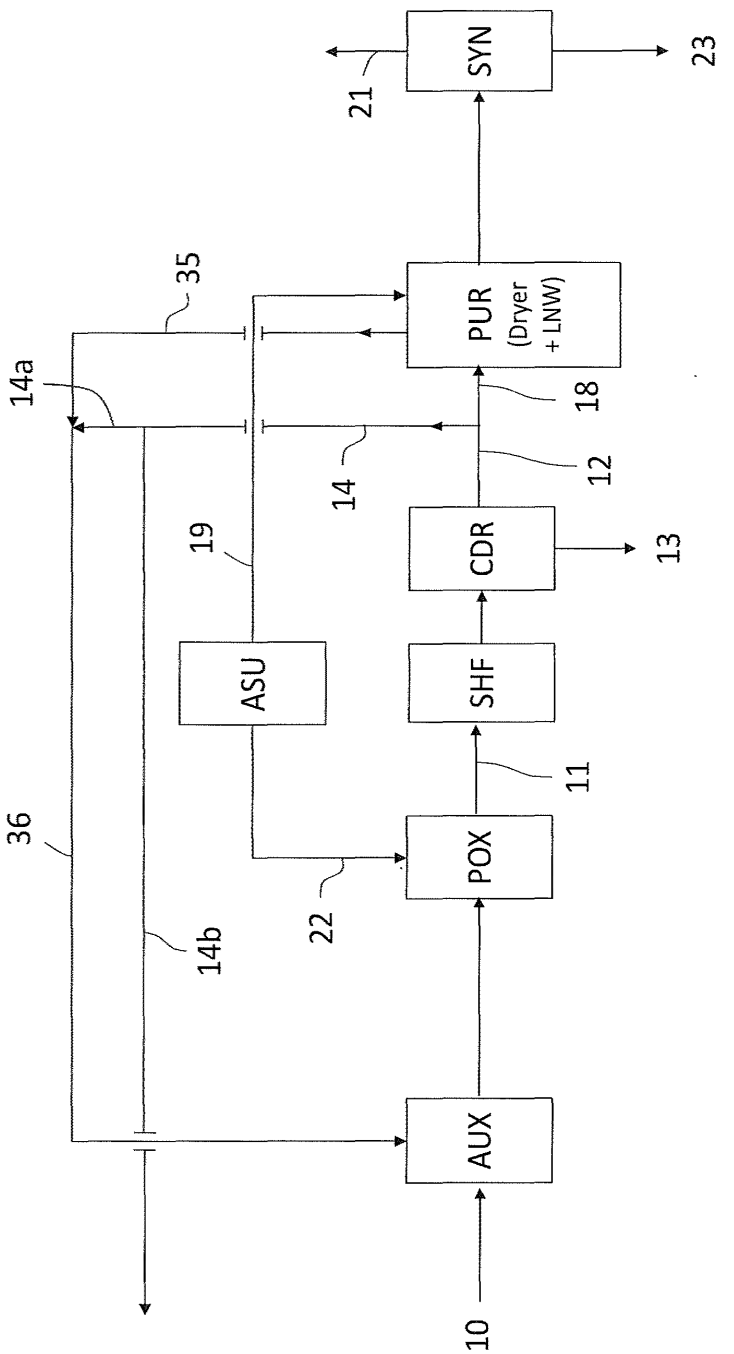

SYN
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23
PUR
(Dryer
+ LNW)
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14a
18
14
12
CDR
19
13
ASU
SHF
11
36
POX
22
14b
AUX
10

FIG. 4

Information on Search Strategy - Pilot phase (see OJ 2015, A86)
The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number
PCT/EP2018/052358

TITLE: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

APPLICANT: CASALE SA

IPC CLASSIFICATION: C01B3/02, C01B3/36, C01C1/04

EXAMINER: Werner, Håkan

CONSULTED DATABASES:

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC: C01B3/025, C01C1/04, C01B3/36, C01B2203/0283, C01B2203/068

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:
ammonia syngas
natural gas
carbon dioxide
shift
carbon monoxide
hydrogen
air separation/ASU
oxygen
oxygen enriched

EPO FORM P04A42

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92*bis*.1 and Administrative Instructions, Section 422)

To:

ZARDI, Marco
c/o M. ZARDI & Co SA
Via Pioda, 6
6900 Lugano

Date of mailing *(day/month/year)*
25 July 2018 (25.07.2018)

Applicant's or agent's file reference
AMC121BWO

IMPORTANT NOTIFICATION

International application No.
PCT/EP2018/052358

International filing date *(day/month/year)*
31 January 2018 (31.01.2018)

1. The following indications appeared on record concerning:

☐ the applicant ☒ the inventor ☐ the agent ☐ the common representative

Name and Address
BARATTO, Francesco
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22100 Como
Italy

State of Nationality | State of Residence

Telephone No.

Facsimile No.

E-mail address

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address
BARATTO, Francesco
Viale Varese 83
22100 Como
Italy

State of Nationality | State of Residence

Telephone No.

Facsimile No.

E-mail address
☐ Notifications by e-mail authorized

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office
☒ the International Searching Authority
☐ the Authority(ies) specified for supplementary search
☒ the International Preliminary Examining Authority
☐ the designated Offices concerned
☐ the elected Offices concerned
☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
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Information on Search Strategy - Pilot phase (see OJ 2015, A86)
The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number
PCT/EP2018/052358

TITLE: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

APPLICANT: CASALE SA

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EXAMINER: Werner, Håkan

CONSULTED DATABASES:

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC: C01B3/025, C01C1/04, C01B3/36, C01B2203/0283, C01B2203/068

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:
ammonia syngas
natural gas
carbon dioxide
shift
carbon monoxide
hydrogen
air separation/ASU
oxygen
oxygen enriched

EPO FORM P04A42

Europäisches Patentamt
European Patent Office
Office européen des brevets

Bescheinigung	Certificate	Attestation
Die angehefteten Unterlagen stimmen mit der als ursprünglich eingereicht geltenden Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.	The attached documents are exact copies of the text in which the European patent application described on the following page is deemed to have been filed.	Les documents joints à la présente attestation sont conformes au texte, considéré comme initialement déposé, de la demande de brevet européen qui est spécifiée à la page suivante.

Patentanmeldung Nr.	**Patent application No.**	**Demande de brevet n°**
	17195305.2 / EP17195305	

The organisation code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP17195305.

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le President de l'Office européen des brevets
p.o.

V. Joseph

Topsoe, Inc. – EX1002
Page 155 of 356

Anmeldung Nr:
Application no.: 17195305.2
Demande no :

Anmeldetag:
Date of filing: 06.10.17
Date de dépôt :

Anmelder / Applicant(s) / Demandeur(s):

CASALE SA
Via Giulio Pocobelli 6
6900 Lugano/CH

Bezeichnung der Erfindung / Title of the invention / Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, oder falls die Anmeldung in einer Nicht-Amtssprache des EPA eingereicht wurde, siehe Beschreibung bezüglich ursprünglicher Bezeichnung.
If no title is shown, or if the application has been filed in a non-EPO language, please refer to the description for the original title.
Si aucun titre n'est indiqué, ou si la demande a été déposée dans une langue autre qu'une langue officielle de l'OEB, se référer à la description pour le titre original.)

In Anspruch genommene Priorität(en) / Priority(Priorities) claimed / Priorité(s) revendiquée(s)
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Topsoe, Inc. – EX1002
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Processo per la sintesi dell'ammoniaca a basse emissioni in atmosfera di CO2

Campo di applicazione

L'invenzione riguarda il settore degli impianti per la sintesi dell'ammoniaca alimentati a gas naturale (NG).

Arte nota

Gli impianti per la sintesi dell'ammoniaca del tipo qui considerato prevedono una sezione atta a convertire il gas naturale in un gas di make-up contenente idrogeno e azoto, e una sezione di sintesi in cui detto gas di make-up reagisce cataliticamente ad alta pressione per dare ammoniaca.

La sezione che genera detto gas di make-up è detta in gergo tecnico front-end. Si usa invece il termine back-end per indicare la sezione di sintesi dell'ammoniaca e la rispettiva sezione frigorifera dedicata a raffreddare l'effluente della sezione di sintesi per poter separare l'ammoniaca.

Nel front-end, il gas naturale desolforato è sottoposto a reforming ottenendo un gas contenente essenzialmente idrogeno, monossido di carbonio CO, diossido di carbonio CO2. Detto gas è in seguito sottoposto a reazione di shift che converte CO in CO2; rimozione di CO2 (decarbonatazione) e preferibilmente metanazione.

Il processo di reforming, in un tipo comune di impianti, prevede un reforming primario con vapore e un successivo reforming secondario catalitico con aria (air-fired). Il reformer primario è riscaldato da bruciatori che utilizzano, quale combustibile, una parte del gas naturale disponibile. Nel reformer secondario invece l'effluente del primario brucia grazie al contatto con l'ossigeno contenuto nell'aria. In alcuni impianti si utilizzano altre configurazioni di reforming, per esempio un reformer autotermico (ATR) preceduto da un forno di riscaldo della carica, cioè della miscela gassosa alimentata a detto reformer.

I descritti impianti ammoniaca hanno notevoli emissioni di CO2 in atmosfera, complessivamente dell'ordine di 100 milioni di tonnellate di CO2 all'anno. Una delle fonti principali di emissione di CO2 è rappresentata dai fumi di combustione del reformer primario e di eventuali altri forni bruciatori, per esempio riscaldatori ausiliari.

Per ragioni ambientali, occorre minimizzare le emissioni di CO2 dai fumi degli impianti NH3. Il problema affligge in particolare gli impianti ammoniaca più datati che sono meno efficienti dei nuovi e hanno maggiori emissioni di CO2 a camino in rapporto alla quantità di ammoniaca prodotta. È altresì necessario che la riduzione delle emissioni non aumenti troppo il costo di produzione dell'ammoniaca.

Allo stato dell'arte, i processi per la cattura di CO2 da fumi si basano su lavaggio con solventi (ad es. il solvente KS-1™ di Mitsubishi). I relativi impianti sono però costosi e complicati, hanno un alto consumo energetico, necessitano del solvente che è costoso. Pertanto questi processi di cattura della CO2 non sono applicabili negli impianti qui considerati dato che alzerebbero troppo il costo di produzione dell'ammoniaca.

In alcuni processi per la sintesi di ammoniaca dell'arte nota, parte del combustibile può essere fornita da una corrente di spurgo proveniente ad esempio da una sezione di purificazione criogenica del gas di sintesi o da un'unità PSA. Detta corrente di spurgo può avere un ridotto contenuto di CO2. Tuttavia, il contributo di detta corrente di spurgo rispetto al combustibile totale è piccolo e non risolve il problema delle emissioni di CO2 in atmosfera.

Sommario dell'invenzione

Lo scopo dell'invenzione è di mettere a disposizione una tecnica per realizzare processi di sintesi dell'ammoniaca con emissioni di CO2 in atmosfera fortemente ridotte rispetto all'arte nota. Un altro scopo dell'invenzione è di mettere a disposizione una tecnica per ammodernare gli impianti esistenti, del

tipo con reformer secondario alimentato ad aria, in grado di ridurre drasticamente le emissioni di CO2 in atmosfera.

Gli scopi sono raggiunti con un processo e con un metodo di ammodernamento (revamping) secondo le rivendicazioni.

Secondo l'invenzione, un processo di sintesi dell'ammoniaca da gas naturale comprende:

conversione di una carica di gas naturale desolforato e vapore, con aria arricchita in ossigeno o con ossigeno, a formare un gas di sintesi contenente idrogeno, CO e CO2;

un trattamento di detto gas di sintesi comprendente almeno una reazione di shift del monossido di carbonio in CO2, e successiva separazione di CO2 dal gas, così ottenendo un gas di sintesi a ridotto contenuto di CO2 e una corrente gassosa ricca di CO2, contenente il CO2 separato dal gas;

opzionalmente, una fase di metanazione del gas di sintesi e/o una aggiunta di azoto al gas di sintesi, ottenendo un gas di make-up contenente azoto e idrogeno in opportuno rapporto molare per la sintesi di ammoniaca,

caratterizzato da:

separazione di una parte di detto gas di sintesi a ridotto contenuto di CO2 ottenendo una quota combustibile del gas di sintesi, in cui detta quota combustibile è alimentata come combustibile a almeno un forno.

L'invenzione ha per oggetto anche un metodo di ammodernamento di un impianto originariamente comprendente una sezione di reforming che include un reformer primario con vapore e reformer secondario ad aria (air-fired), e trattamento del gas di sintesi comprendente shift di monossido di carbonio in diossido di carbonio, decarbonatazione e eventualmente metanazione. Il metodo di ammodernamento comprende almeno:

fornire una corrente di aria arricchita, o di ossigeno, e utilizzare detta corrente quale ossidante per il reformer secondario al posto dell'aria;

separare una quota parte del gas di sintesi a valle della decarbonatazione,

alimentare detta parte del gas di sintesi, avente un ridotto contenuto di CO2, come combustibile per almeno un forno dell'impianto.

Con il termine di forno si intende un apparecchio tra: un reformer a vapore (steam reformer) o un preriscaldatore della carica o un generatore di vapore o un surriscaldatore di vapore. Questi apparecchi, che operano con una combustione, sono identificati con il termine "fired heater". Detto forno in alcune realizzazioni è parte della sezione di conversione del gas naturale in gas di sintesi. Negli impianti combinati ammoniaca-urea detto forno può essere parte della sezione urea.

La parte di gas di sintesi separata, e inviata a detto almeno un forno, è definita quota di combustibile (quota fuel) del gas disponibile dopo la fase di shift. Preferibilmente detta quota fuel è compresa tra 1% e 40% del gas disponibile, più preferibilmente tra 10% e 30% e ancora più preferibilmente tra 20% e 30%. Per esempio in una realizzazione preferita la quota fuel è pari al 30%. La restante parte, che è destinata alla conversione in ammoniaca, è denominata quota di processo.

Si deve notare che detta quota fuel è relativamente alta, per esempio circa 1/3 del totale. L'invenzione infatti prevede di destinare a combustibile una porzione non trascurabile di gas di sintesi, per ridurre le emissioni di CO2. Ciò comporta la necessità di produrre una quantità aggiuntiva di gas di sintesi ma, come sarà meglio spiegato nel seguito con l'aiuto degli esempi, questa necessità è compensata dai vantaggi dell'invenzione.

La separazione della quota combustibile, vantaggiosamente, è effettuata con una diramazione (split) di una corrente di processo, per esempio di gas di processo dopo shift e decarbonatazione. Per effetto di detta diramazione, la

quota combustibile e la restante parte del gas, detta anche quota di processo, hanno la medesima composizione.

Si deve notare che la presente invenzione prevede di destinare deliberatamente una parte della corrente di processo alla quota combustibile, la quota combustibile essendo separata direttamente dalla corrente di processo e avente la medesima composizione. L'arte nota, al contrario, insegna solo a destinare come combustibile le eventuali correnti di spurgo, derivanti da processi di purificazione e contenenti metano.

Il menzionato gas di sintesi a ridotto contenuto di CO2 (CO2-depleted syngas) preferibilmente contiene non più di 1000 ppm in volume (0.1%) di CO2. Detto gas è composto essenzialmente da idrogeno (H_2) con eventuali piccole quantità residue di CO e di CH4, tipicamente meno di 2% in volume e preferibilmente meno di 1%.

La combustione di detto gas è sostanzialmente libera da produzione di CO2. Infatti la combustione dell'idrogeno non forma CO2, e solo la piccola quantità di CO o di CH4, eventualmente presente, può formare CO2.

L'invenzione suggerisce di utilizzare una parte di gas di processo come combustibile per uno o più forni della sezione di reforming, contrariamente all'arte nota che, a questo scopo, utilizza parte del gas naturale, cioè un idrocarburo. Questa parte di gas di processo (quota fuel) è separata opportunamente dopo un trattamento di rimozione di CO2 e, come spiegato più sopra, contiene essenzialmente idrogeno che può bruciare senza formare CO2. Di conseguenza si comprende che l'invenzione consente di ridurre drasticamente le emissioni di CO2 in atmosfera.

Detta aria arricchita in ossigeno preferibilmente contiene almeno il 50% di ossigeno in volume e più preferibilmente almeno il 90% di ossigeno in volume e ancora più preferibilmente almeno il 95%. I vantaggi di un elevato contenuto di ossigeno nell'aria arricchita sono: maggiore potere calorifico del gas di sintesi; minore portata di gas di scarico (flue gas) a camino; minore portata volumetrica

attraverso gli apparecchi della sezione di conversione e, di conseguenza, apparecchi più piccoli.

Il gas di sintesi a ridotto contenuto di CO2 preferibilmente costituisce tutto, o sostanzialmente tutto, il combustibile dei forni utilizzati per il processo. In alcune realizzazioni tuttavia si preferisce mantenere una piccola quantità di gas naturale che è denominata "trim fuel" del forno. Preferibilmente detta piccola quantità ha un contributo al calore di combustione totale del forno (duty) non superiore al 15%, più preferibilmente non superiore al 10%. Il trim fuel consente di controllare rapidamente il forno, per esempio per alzare o abbassare il carico velocemente in caso di necessità.

Detto contributo al calore di combustione è esprimibile come il prodotto tra portata (kg/s o mol/s) e potere calorifico (J/kg o J/mol).

Alcune realizzazioni dell'invenzione prevedono una metanazione del gas di sintesi a valle della decarbonatazione. La fase di metanazione converte CO e CO2 residui in CH4, consumando H2, in accordo alle reazioni $CO + 3H_2 \rightarrow CH_4 + H_2O$ e $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$.

Preferibilmente, la separazione della quota fuel dal gas di sintesi a ridotto contenuto di CO2 avviene prima (a monte) di detta fase di metanazione.

Il vantaggio di separare la quota fuel prima della metanazione è di non sovradimensionare la sezione di metanazione della quota fuel, e di non perdere il calore di metanazione della quota fuel. Inoltre a parità di calore richiesto dal forno e di temperatura del gas, la quota fuel è leggermente minore se prelevata prima della metanazione.

Non c'è svantaggio dal punto di vista delle emissioni di CO2 in atmosfera, che sono le stesse sia usando come combustibile il gas a monte del metanatore, che a valle del metanatore, a parità di portata. Se è prevista una aggiunta di azoto, la quota fuel è separata prima di detta aggiunta di azoto. Il vantaggio è un maggiore potere calorifico del gas di sintesi usato come combustibile, che non contiene l'azoto, o ne contiene di meno.

Dopo aver separato la quota fuel, il gas di sintesi a ridotto contenuto di CO2 può essere opzionalmente trattato in una sezione di purificazione comprendente per esempio una unità PSA o comprendente un essiccatore seguito da una unità criogenica.

La sezione di purificazione produce almeno una corrente di gas di sintesi per l'ammoniaca a ridotto contenuto di inerti, ed almeno una corrente di scarto contenente CO, e CH4. La corrente di scarto può contenere anche H2 ed N2. In alcune realizzazioni, almeno una parte del gas di scarto di detta sezione di purificazione è usata come combustibile insieme alla quota fuel. Di conseguenza, la quota fuel può essere diminuita.

Il vantaggio dell'unità di purificazione è di ridurre il contenuto di inerti nel make-up gas, che comporta vantaggi noti per la sintesi dell'ammoniaca, tra cui un minor consumo per la circolazione e una riduzione (o addirittura eliminazione) della portata di spurgo del loop di sintesi ammoniaca.

L'invenzione, vantaggiosamente, prevede di separare la quota fuel a monte dell'unità di purificazione. Di conseguenza, solo la porzione di gas di sintesi inviata alla sintesi di ammoniaca è sottoposta a trattamento nella sezione di purificazione che, non dovendo processare il gas di sintesi corrispondente alla quota fuel, può essere realizzata con dimensioni molto inferiori. Il vantaggio di separare la quota fuel a monte dell'unità di purificazione è di non sovradimensionare l'unità di purificazione ed i relativi consumi per la quota fuel del gas di sintesi. Un altro vantaggio è la possibilità di controllare indipendentemente la quota fuel e l'unità di purificazione.

Non c'è svantaggio a separare la quota fuel a monte della purificazione dal punto di vista delle emissioni di CO2 in atmosfera, perché il CO, CO2 e CH4 contenuti nel gas di sintesi della quota fuel sarebbero separati dall'unità di purificazione a formare la corrente di scarto, ed usati come combustibile.

Vantaggiosamente, l'unità di purificazione non deve avere un recupero di idrogeno eccessivamente elevato, perché l'idrogeno "perso" nel gas di scarto è

usato come combustibile e non comporta emissioni di CO2 in atmosfera. La quota fuel del gas di sintesi è conseguentemente regolata.

Preferibilmente, però, l'unità di purificazione ha un recupero di idrogeno sufficientemente elevato perché la quota fuel contribuisca per almeno il 30%, preferibilmente almeno il 40%, ancor più preferibilmente almeno il 50% del duty del forno. La richiedente ha trovato che tale condizione è vantaggiosa per il controllo del forno stesso indipendentemente dal controllo dell'unità di purificazione.

La sezione di purificazione può comprendere adsorbimento selettivo dei componenti indesiderati su solido. In alcune realizzazioni detta sezione di purificazione comprende una unità pressure swing adsorption (PSA) che utilizza setacci molecolari per separare CO, CH4, Ar, H2O e CO2 residuo. In altre realizzazioni detta sezione comprende almeno un essiccatore (dryer) per la separazione di CO2 residuo e acqua, seguito da un'unità di separazione criogenica per la separazione di CO, CH4 e Ar. L'unità di separazione criogenica preferibilmente è una unità di lavaggio con azoto liquido (unità Liquid Nitrogen Wash o LNW).

Una unità PSA tipicamente produce una sola corrente di prodotto purificato, sostanzialmente alla pressione dell'alimentazione, ed una sola corrente di gas di scarto, a pressione molto più bassa dell'alimentazione. Detta corrente di scarto contiene CO, CH4, Ar, H2O e la CO2 residua, e può contenere H2 ed N2.

Se la sezione di purificazione comprende dryer e LNW, il prodotto purificato può emergere come una o più correnti, e può già contenere H2 ed N2 in rapporto adeguato per la sintesi dell'ammoniaca.

Il dryer ha un gas di coda, prodotto della rigenerazione dei setacci molecolari usati per catturare principalmente H2O e le tracce di CO2 residua contenute nell'alimentazione, che congelebbero durante il trattamento criogenico nella unità LNW. Il dryer può essere rigenerato con un flusso di azoto (proveniente

dall'unità di separazione aria), in questo caso il gas di coda (tail gas) contenente N2, H2O e CO2 può essere scaricato in atmosfera, oppure combinato con il tail gas del LNW descritto dopo.

Il LNW ha pure almeno un gas di coda che comprende ilprodotto di fondo della colonna di assorbimento del LNW, contenente CH4 e CO, oltre ad N2 e H2. Il gas di scarto del LNW può essere inviato come combustibile.

Il tail gas del LNW può essere usato almeno in parte per la rigenerazione del dryer prima di essere inviato come combustibile.

Il gas di sintesi a ridotto contenuto di inerti può essere inviato alla sintesi di ammoniaca.

La metanazione è una reazione esotermica, ma il calore di reazione non è sostanzialmente grande ed usualmente non è recuperato.

La metanazione pertanto lascia una piccola quantità di metano nel gas di sintesi (slip di metano). La presenza di dette piccole quantità di metano nel gas di sintesi non è un problema ai fini della produzione dell'ammoniaca essendo il metano inerte nei confronti della reazione di sintesi. Il metano si accumula nello spurgo del loop di sintesi. Tuttavia usando lo spurgo del loop di sintesi come combustibile, il metano in esso contenuto rappresenta una sorgente di CO2, sebbene di piccola entità.

Anche il monossido di carbonio contenuto nel gas di sintesi rappresenta una sorgente di CO2, sebbene di piccola entità, sia per effetto della combustione del gas di sintesi usato come combustibile, sia per effetto della combustione del gas di scarto dell'eventuale unità di purificazione.

In alcune realizzazioni dell'invenzione, per ridurre anche questa fonte di CO2 (cioè le emissioni dovute alla presenza di monossido di carbonio residuo del gas di sintesi) il processo comprende una purificazione catalitica atta a convertire selettivamente il CO a CO2 a monte della decarbonatazione. Una conversione selettiva del monossido di carbonio per esempio è ottenibile con il

processo noto come Selectoxo™ che opera con la reazione CO + 1/2 O2 → CO2. L'ossigeno per l'ossidazione selettiva del CO può essere una parte della menzionata corrente di aria arricchita o ossigeno.

Un vantaggio di detta conversione selettiva di CO a CO2 è che almeno parte del CO residuo dallo shift è convertito in CO2 e rimosso nella decarbonatazione. Di conseguenza la combustione del gas di sintesi, dello spurgo del loop di sintesi, o del gas di scarto dell'eventuale purificazione, produce una minore quantità di CO2.

Secondo l'invenzione, le emissioni di CO2 a camino sono determinate principalmente dal contenuto di CO, CO2 e CH4 del gas di sintesi a valle della decarbonatazione, oltre che dalla corrente di trim fuel opzionale che sarà descritta nel seguito.

La combustione di detto gas è sostanzialmente libera da produzione di CO2. Infatti la combustione dell'idrogeno non forma CO2, e solo la piccola quantità di CO o di CH4, eventualmente presente, può formare CO2.

La produzione di CO2 deriva anche dalla combustione del metano contenuto nello spurgo del loop di sintesi.

In caso di unità di purificazione, la produzione di CO2 deriva anche dalla combustione di CO, CH4 e CO2 residua del gas di scarto.

Un aspetto dell'invenzione prevede che la quota fuel sia prodotta in quantità in eccesso rispetto al combustibile necessario per la sezione di conversione, la quantità di detta quota fuel eccedente la richiesta essendo esportata dal processo, e la regolazione della sezione di conversione sia operata modulando la quantità di detta quota fuel diretta alla sezione di conversione e la quantità esportata dal processo.

La conversione del gas naturale in gas di sintesi può avvenire con diverse tecniche.

Alcune realizzazioni dell'invenzione prevedono che la fase di conversione del gas naturale in gas di sintesi comprenda un reforming primario seguito da reforming secondario.

Alcune realizzazioni, più preferibilmente, prevedono che la fase di conversione comprenda un reforming autotermico catalitico (ATR), opzionalmente preceduto da un reforming preliminare (pre-reforming). Un ATR privo di reforming preliminare è detto anche "ATR puro". Vantaggiosamente, in queste realizzazioni, almeno una parte della quota fuel di gas di sintesi alimenta un forno di pre-riscaldo del gas prima del reforming autotermico.

Il vantaggio di usare un ATR, puro o in combinazione con un pre-reformer, consiste nel minor calore richiesto del forno rispetto alla combinazione dell'ATR con un reformer primario, anche considerando il calore richiesto per la generazione e surriscaldo di vapore necessario per il processo. Ciò è dovuto al fatto che la temperatura di preriscaldo dell'alimentazione dell'ATR e dell'eventuale prereformer secondo l'invenzione è opportunamente scelta ad un valore non superiore a 650°C, inferiore alla temperatura di uscita del reformer primario, ed al fatto che nel forno di preriscaldo non si ottiene alcun avanzamento della reazione di steam reforming (endotermica).

Un ATR puro, o ATR in combinazione con un prereformer, può vantaggiosamente operare con un rapporto vapore/carbonio (S/C) più basso di un reformer primario. Preferibilmente detto rapporto S/C è non superiore a 2, più preferibilmente non superiore a 1.5, ancor più preferibilmente non superiore a 1. Anche questo contribuisce a ridurre il calore rischiesto dal forno di preriscaldo dell'alimentazione dell'ATR e dell'eventuale prereformer.

Nel caso di ATR senza reformer primario, la quota fuel è preferibilmente compresa tra 1 e 30%, più preferibilmente tra il 10 e il 30%, ancora più preferibilmente tra il 10 e il 20%.

In alcune realizzazioni la fase di conversione del gas naturale in gas di sintesi comprende una fase di ossidazione parziale non catalitica (POX).

Vantaggiosamente in queste realizzazioni almeno una parte della quota fuel di gas di sintesi alimenta un forno di pre-riscaldo del gas prima di detta ossidazione parziale non catalitica, oppure per generazione di vapore o per surriscaldamento di vapore.

Il vantaggio di usare un POX consiste nel minor calore richiesto del forno rispetto alla combinazione di un ATR con un reformer primario, anche considerando il calore richiesto per la generazione e surriscaldo di vapore necessario per il processo. Ciò è dovuto al fatto che la temperatura di preriscaldo dell'alimentazione del POX secondo l'invenzione è opportunamente scelta ad un valore non superiore a 500°C, nettamente inferiore alla temperatura di uscita del reformer primario, ed al fatto che nel forno di preriscaldo non si ottiene alcun avanzamento della reazione di steam reforming (endotermica).Inoltre il POX può vantaggiosamente usare un rapporto S/C più basso di un reformer primario, preferibilmente non superiore a 2, più preferibilmente non superiore a 1, ancor più preferibilmente non superiore a 0.5. Anche questo contribuisce a ridurre il calore rischiesto dal forno di preriscaldo.

Nel caso di POX, la quota fuel è preferibilmente compresa tra 1 e 30%, più preferibilmente tra il 10 e il 30%, ancora più preferibilmente tra il 10 e il 20%.

La diminuzione del calore richiesto dal forno di preriscaldo per un POX e per un ATR puro rispetto ad un ATR in combinazione a reformer primario comporta i seguenti vantaggi: la quota fuel del gas di sintesi è minore, ed è possibile diminuire la quantità di trim fuel, pertanto si possono ottenere minori emissioni di CO2 a camino.

Sia nel caso di POX con unità di purificazione opzionale del gas di sintesi sia nel caso di ATR senza reformer primario con unità di purificazione opzionale del gas di sintesi, è preferibile selezionare un'unità di purificazione ad alto recupero di idrogeno, per esempio un liquid nitrogen wash, per ottenere che la quota fuel del gas di sintesi sia sufficientemente grande per controllare il forno indipendentemente dal controllo dell'unità di purificazione.

Un altro vantaggio del POX e dell'ATR senza reformer primario, conseguenza sia della minore quota fuel che del minore rapporto vapore carbonio, è la minore produzione autogena di vapore, che riduce il calore richiesto per il relativo surriscaldo, la quota fuel, le emissioni di CO2 a camino ed il consumo totale di gas naturale.

La minore produzione autogena di vapore può determinare una carenza di vapore per movimentare le turbine o di elettricità per alimentare i motori delle macchine. L'energia mancante può essere convenientemente importata dall'esterno dell'impianto come elettricità a ridotte emissioni di CO2, per esempio generata da fonti rinnovabili. Si deve osservare che questa sinergia non è possibile se il processo produce già un eccesso di vapore o energia, per esempio nel caso di combinazione di primario ed ATR con una quota fuel piuttosto grande.

In alcune realizzazioni la fase di conversione del gas naturale in gas di sintesi comprende anche una fase di reforming con vapore (steam reforming). Vantaggiosamente in queste realizzazioni almeno una parte della quota fuel di gas di sintesi alimenta i bruciatori del reformer.

Una parte della quota fuel può essere destinata, in alcune realizzazioni, a forni per la produzione e/o surriscaldo di vapore.

L'invenzione consente anche di produrre l'elettricità necessaria per il processo di sintesi dell'ammoniaca o dei suoi derivati (per esempio l'urea) con basse emissioni di CO2, mediante l'utilizzo come combustibile del gas di sintesi avente un ridotto contenuto di CO2, per esempio nei seguenti modi:

- espansione in turbogeneratore di una corrente di vapore prodotta in un generatore di vapore o surriscaldatore di vapore, alimentato come combustibile dal gas di sintesi avente un ridotto contenuto di CO2;

- combustione in una turbina a gas, o in un motore a gas (gas engine), alimentato come combustibile dal gas di sintesi avente un ridotto contenuto di CO2.

Generalmente nei processi ammoniaca si estrae dal processo (loop) di sintesi dell'ammoniaca un gas di spurgo, al fine di rimuovere gli inerti dal loop di sintesi, e detto gas di spurgo è trattato con un processo di recupero dell'idrogeno in esso contenuto (HRU). Detto processo di recupero genera un gas ricco di idrogeno che può essere riutilizzato per la sintesi, e un gas di coda (tail gas) contenente la maggior parte del metano inizialmente contenuto nel gas di spurgo. Il metano nel gas di coda è praticamente tutto quello contenuto nella quota di processo del gas di sintesi. Normalmente detto gas di coda, dato il suo contenuto relativamente alto di metano, è usato esclusivamente come combustibile. Questo utilizzo del gas di coda tuttavia genera emissioni di CO2.

Un aspetto dell'invenzione prevede di riciclare almeno una parte di detto gas di coda come gas di processo nella fase di conversione del gas naturale, ad esempio nella fase di reforming o ossidazione parziale. Un vantaggio connesso è una ulteriore diminuzione delle emissioni di CO2.

In alcune realizzazioni una parte del detto gas di sintesi a ridotto contenuto di CO2 è trattata in un'unità per separare azoto (N2), preferibilmente una unità a membrana, ottenendo un gas di sintesi a ridotto contenuto di azoto e una corrente ricca di azoto; almeno una parte del gas di sintesi a ridotto contenuto di azoto (preferibilmente tutto) è utilizzata come combustibile; la restante parte è alimentata alla sintesi dell'ammoniaca insieme alla corrente ricca di azoto.

Questa configurazione è particolarmente vantaggiosa se l'aria arricchita in O2 non ha una purezza elevatissima (ad esempio inferiore a 95% di O2), e/o se il gas naturale contiene azoto. Si ottengono tre benefici: di aumentare il potere calorifico del fuel gas, di ridurre la portata di fumi di combustione (e la potenza del rispettivo ventilatore, detto ID fan), e di conservare l'azoto che è un reagente per l'ammoniaca. L'unità di separazione dell'azoto a membrana è ulteriormente preferita perché detta unità può operare sfruttando la differenza di pressione tra il gas di sintesi (prodotto a elevata pressione) e la combustione nel forno (che avviene a pressione atmosferica). Inoltre la corrente ricca di azoto, che va alla sintesi, non perde pressione.

La configurazione appena descritta, che prevede separazione dell'azoto dal gas di sintesi, è applicabile anche in un processo convenzionale, con steam reformer primario e reformer secondario ad aria, ottenendo il vantaggio di non dover modificare o ingrandire il compressore aria. Tuttavia con un secondario ad aria, e senza modificare il compressore e quindi non potendo aumentare la portata di aria, si dovrebbe produrre la quota aggiuntiva di gas di sintesi (richiesto come fuel) aumentando la capacità del reformer primario e/o installando un reformer riscaldato a gas (GHR), entrambe le soluzioni essendo molto costose. Per questi motivi la descritta separazione dell'azoto è particolarmente preferita in combinazione all'uso dell'aria arricchita nella fase di conversione del gas naturale in gas di sintesi.

In alcune realizzazioni, è prevista una espansione, con produzione di lavoro meccanico, del gas di sintesi a ridotto contenuto di CO2 dopo averlo opzionalmente scaldato.

Detto gas è disponibile a una pressione maggiore della pressione richiesta per la combustione in forno, pertanto può essere espanso in una macchina adeguata, come un espansore o una turbina, producendo lavoro meccanico. Per esempio detta espansione può essere da circa 25 a circa 3 bar. Il gas ha un volume specifico elevato dato che comprende essenzialmente H_2, e per questo la sua espansione può generare una potenza ragguardevole. La potenza ottenuta può coprire in parte i fabbisogni del processo, rendendolo più efficiente.

In alcune realizzazioni la fase di shift comprende due fasi a diversa temperatura, per esempio preferibilmente uno shift ad alta temperatura (HTS) per esempio su catalizzatore a base Ferro seguito da uno shift a bassa temperatura (LTS) o a media temperatura (MTS) per esempio su catalizzatore a base Rame. Il vantaggio correlato è di ottenere la massima conversione del CO in CO2, che sarà poi separata nella fase di decarbonatazione, in modo da avere il minimo contenuto residuo di CO nel gas di sintesi utilizzato come combustibile. Dato che il CO è una fonte di CO2, durante la combustione, si ottiene il vantaggio di minimizzare le emissioni di CO2 a camino.

In alcune realizzazioni, in cui si utilizza un S/C globale relativamente basso, per esempio <2.7, la fase di shift comprende preferibilmente due fasi in serie svolte su catalizzatore adatto a operare con basso tenore di vapore, per esempio catalizzatore a base Rame. In questa configurazione, la prima fase è costituita da uno shift a media temperatura (MTS) preferibilmente pseudo-isotermo operante nel range di temperatura 200-320°C, e la seconda è uno shift a bassa temperatura (LTS) operante nel range di temperatura 180-250°C.

La conversione del gas naturale in gas di sintesi, ad esempio tramite reforming, avviene preferibilmente a pressione inferiore a 50 bar, più preferibilmente inferiore a 40 bar, più preferibilmente inferiore a 30 bar.

Generalmente l'arte nota insegna a privilegiare pressioni di conversione alte, per aumentare la capacità della sezione di conversione (front-end) e per ridurre il consumo della compressione del gas di sintesi. La presente invenzione invece è preferibilmente messa in opera con pressioni di conversione basse per ottenere la massima conversione del metano, perché la reazione di steam reforming è favorita a pressione inferiore, in modo da avere il minimo contenuto residuo di metano nel gas di sintesi utilizzato come combustibile. Dato che il metano è una fonte di CO2, durante la combustione, si ottiene il vantaggio di minimizzare le emissioni di CO2 a camino.

Nel caso di ATR, un'alta conversione di metano è anche ottenuta operando a temperatura di uscita relativamente alta, >950°C, preferibilmente >1000°C, ancor più preferibilmente > 1030°C.

Nel caso di POX, un'alta conversione di metano è anche ottenuta operando a temperatura di uscita relativamente alta, >1200°C, preferibilmente >1300°C.

In alcune realizzazioni il rapporto vapore/carbonio (steam to carbon, S/C) globale nella fase di conversione è maggiore di 2.0, preferibilmente maggiore di 2.4 e più preferibilmente maggiore di 2.7. Generalmente l'arte nota insegna a privilegiare S/C bassi per aumentare la capacità della sezione di conversione (front-end). L'invenzione in contrasto prevede un rapporto S/C relativamente

alto per massimizzare la conversione del metano, e del CO nella fase di shift, e ridurre la concentrazione di CH4 e CO nel gas di sintesi. Dato che il metano e CO sono una fonte di CO2, durante la combustione, si ottiene il vantaggio di minimizzare le emissioni di CO2 a camino.

In caso di ATR puro (eventualmente in combinazione con prereformer) o di POX, l'invenzione adotta nella sezione di reforming un S/C non superiore a 2. Preferibilmente ulteriore vapore è aggiunto a valle del reforming e a monte dello shift, fino al raggiungimento di un S/C globale >2, preferibilmente >2.4 per promuovere l'avanzamento della reazione di shift e la relativa conversione del monossido di carbonio.

L'uso del trim fuel risolve il problema di controllare rapidamente il forno ma a prezzo di aumentare le emissioni di CO2 in atmosfera. Per alcune configurazioni dell'invenzione, per esempio quelle comprendenti uno steam reformer, il trim fuel è il maggiore contributo alle emissioni di CO2 in atmosfera. Questo sarà mostrato negli esempi.

In una realizzazione preferita dell'invenzione, il trim fuel non è utilizzato, ed il combustibile del forno è solo il gas di sintesi. La quota fuel è conseguentemente maggiore rispetto al caso in cui si utilizzi il trim fuel, perché occorre fornire anche il calore di combustione del trim fuel con la quota fuel.

In una prima realizzazione, la quota fuel ha un calore di combustione sostanzialmente corrispondente al calore richiesto dal forno. Per controllare rapidamente il forno, per esempio per alzare o abbassare il carico velocemente in caso di necessità, la portata della quota fuel è adeguatamente alzata o abbassata. Questo controllo, però, ha la conseguenza indesiderata di variare la portata del gas di make-up, e quindi la produzione. Per ristabilire la produzione iniziale, occorre aumentare o diminuire la portata totale di gas naturale alimentata al reforming, che a sua volta richiede un controllo del forno. Si può comprendere come questa procedura sia operativamente indesiderata.

Un aspetto dell'invenzione prevede che: la quota fuel è prodotta in quantità sovrabbondante rispetto alla richiesta di detto almeno un forno, cioè è prodotto un surplus di gas di sintesi da usare come combustibile rispetto alla quantità corrispondente al calore richiesto dal forno, ed il surplus di gas di sintesi combustibile è esportato dal processo, cioè non è usato né come quota fuel né come quota di processo. La disponibilità di gas di sintesi (da usarsi come combustibile) in eccesso consente di regolare rapidamente detto almeno un forno senza utilizzare, o utilizzando in quantità minore, il trim fuel, con ulteriore vantaggio in termini di riduzione delle emissioni di CO2.

Per esempio, il surplus può essere:

- esportato come ulteriore prodotto (per esempio come idrogeno, o come combustibile privo di CO2 per consumi esterni all'impianto ammoniaca), oppure
- inviato ad un polmone di stoccaggio, oppure
- bruciato in torcia.

Per controllare rapidamente il forno, per esempio per alzare o abbassare il carico velocemente in caso di necessità, la portata del surplus di gas di sintesi è adeguatamente abbassata o alzata, senza impattare ne la quota fuel né la quota di processo.

Il surplus di gas di sintesi fuel può essere prelevato dalla quota fuel, ed avere dunque la stessa composizione e pressione del gas di sintesi fuel.

In alternativa, se è presente un'unità di purificazione (per esempio una PSA) o una metanazione, il surplus di gas di sintesi fuel può essere prelevato a valle della purificazione o metanazione, per avere una maggiore purezza del surplus esportato.

Il surplus fuel può essere separato dal gas di coda della purificazione (PSA, oppure dryer + LNW), anche se detta soluzione è meno preferita per due ragioni:

il gas di coda è a bassa pressione, pertanto richiederebbe una compressione per poterlo esportare (con notevole dispendio energetico e costo d'impianto);

il gas di coda contiene CO, CO2 e CH4 in concentrazione molto maggiore sia del gas di sintesi fuel, che del prodotto della purificazione, pertanto ha composizione meno desiderabile.

La quantità del surplus di gas di sintesi combustibile è preferibilmente >2%, più preferibilmente >4%, ancor più preferibilmente >6% della quota fuel. Se il surplus di gas di sintesi combustibile non è esportato, la sua quantità è preferibilmente non superiore a 15% della quota fuel, ancor più preferibilmente non superiore a 10% della quota fuel, per evitarne un consumo eccessivo.

L'invenzione ottiene emissioni di CO2 inferiori a 0.5 t/t (ton di CO2 emessa per ton di ammoniaca prodotta); in realizzazioni preferite dell'invenzione le emissioni sono inferiori a 0.3 t/t, o inferiori a 0.2 t/t.

Come sarà mostrato negli esempi, in alcune realizzazioni preferite le emissioni di CO2 possono raggiungere valori inferiori a 0.1 t/t o addirittura 0.05 t/t, corrispondenti a una cattura prossima al 99% della CO2.

Per quanto riguarda l'impianto, i forni sono vantaggiosamente equipaggiati con bruciatori "dual fuel", adatti a bruciare sia gas naturale sia il gas di sintesi. L'invenzione può richiedere la installazione di una unità di separazione aria (ASU) per produrre l'aria arricchita, e opzionalmente azoto.

L'invenzione può essere applicata anche ai processi e impianti ammoniaca-urea. Un impianto ammoniaca-urea è un impianto comprendente una prima sezione di sintesi di ammoniaca e una seconda sezione di sintesi di urea da ammoniaca e CO2, in cui almeno una parte dell'ammoniaca prodotta nella prima sezione alimenta la seconda sezione. In questo caso anche la CO2 separata nella fase di decarbonatazione alimenta vantaggiosamente detta seconda sezione di sintesi di urea.

I principali vantaggi dell'invenzione sono i seguenti.

La separazione del CO2 avviene da un gas di sintesi che è concentrato in CO2 (15-25% mol) ed è a pressione relativamente alta, pertanto la separazione di CO2 è da questa corrente è molto più agevole e richiede meno consumo di energia rispetto a separate CO2 da fumi di combustione.

Il sistema dell'invenzione non richiede solvente per la cattura di CO2 da fumi.

L'uso di aria arricchita in ossigeno introduce diversi vantaggi:

- aumenta il potere calorifico del gas di sintesi;

- la combustione del gas di sintesi genera meno fumi rispetto alla combustione di gas naturale, a parità di calore rilasciato, perché la combustione di idrogeno (contenuto nel gas di sintesi) avviene con riduzione del numero di moli contrariamente alla combustione del metano, per cui la convettiva del reformer è più piccola e richiede un ventilatore (induced draft fan o ID fan) meno potente;

- limita la perdita a camino di azoto (che è un reagente), evitando uno spreco di energia di separazione e compressione di N2; la generazione di azoto per la sintesi non deve essere ingrandita;

- permette di tenere un'alta temperatura di conversione del gas naturale, libera dal vincolo di non introdurre azoto in eccesso rispetto alla stechiometria della sintesi NH3 (tipico dei processi convenzionali, ad aria) con un'elevata conversione del metano che rende minime le emissioni di CO2.

Negli impianti convenzionali con reformer secondario ad aria, l'aria di processo è alimentata a detto reformer secondario in quantità stechiometrica, cioè nella quantità richiesta per raggiungere un rapporto di H/N circa 3 nel make-up gas. Ciò significa che la portata di aria (in particolare la quantità di ossigeno introdotto nel reformer) non può essere scelta liberamente, ad esempio per raggiungere una conversione completa del NG.

Invece, se l'ossidante e l'azoto sono alimentati separatamente al processo, si può scegliere la portata di ossidante per ottenere una conversione completa del

gas naturale ed eventualmente aggiungere a valle l'azoto che serve per la composizione di make-up gas desiderata. Il vantaggio della conversione completa è di produrre un gas di sintesi con minore contenuto di metano, e quindi minori emissioni di CO2.

Un altro vantaggio dell'invenzione è che la maggiore portata di gas nel frontend permette di recuperare più calore e di generare più vapore. La maggior quantità di vapore prodotto nel frontend limita il carico dei rispettivi apparecchi ausiliari di generazione del vapore; un vantaggio è che il consumo di combustibile (e potenziale sorgente di emissioni di CO2) è rappresentato sostanzialmente solo dal reformer primario o riscaldatore (o fired heater). Sostituendo il combustibile del reformer con gas di sintesi (e se necessario sostituendo i relativi bruciatori) si ottiene un sostanziale abbattimento o annullamento delle emissioni di CO2.

Un altro vantaggio è che l'invenzione non richiede necessariamente di separare idrogeno dal gas di sintesi a ridotto contenuto di CO2, cioè di purificare il gas di sintesi a ridotto contenuto di CO2 in un gas ricco in H2 ed un "waste gas", per ottenere basse emissioni di CO2 in atmosfera. Il gas di sintesi a ridotto contenuto di CO2 si può usare direttamente per la sintesi di ammoniaca dopo eventuale metanazione.

In alcune realizzazioni può essere vantaggioso prevedere una purificazione del gas di sintesi per ridurre il consumo energetico globale del processo.

Quando applicata all'ammodernamento (revamping) di impianti, l'invenzione ottiene notevoli sinergie che permettono di ridurre le emissioni di CO2 senza perdere produzione, limitando modifiche e costi. Questo perché l'invenzione:

- riduce molto la portata di gas nel frontend, e quindi le relative apparecchiature e tubazioni (secondario, shift, decarbonatazione metanazione) sono adatte per una capacità maggiore;

- detta capacità maggiore corrisponde al gas di sintesi da usare come fuel;

- può usare una temperatura alta di uscita dal secondario (ottenendo una conversione completa del metano), perché l'azoto si aggiunge separatamente dall'ossigeno; pertanto il metodo dell'invenzione produce il gas in più da usare come combustibile senza richiedere costose modifiche del reformer primario anche quando detto reformer è sostanzialmente al limite della capacità;

- sbottiglia la sezione di rimozione CO2, perché aumenta la pressione parziale di CO2 e riduce la portata di gas nell'assorbitore;

- la combustione del CO2-depleted syngas genera meno fumi del NG, per cui la convettiva del reformer e ventilatore (ID fan) sono scaricati;

- si deve modificare solo il frontend, mentre il backend (compressore del gas di sintesi, sintesi dell'ammoniaca, sezione frigorifera) è sostanzialmente inalterato;

- il processo non necessita di una purificazione spinta del gas di sintesi per rimuovere gli inerti, essendo sufficiente usare il metanatore (spesso esistente); in particolare, non è necessario alcuno step di separazione del gas di sintesi in una corrente di H2 e gas di scarto (waste gas).

Descrizione delle figure

La Fig. 1 illustra una prima realizzazione dell'invenzione.

La Fig. 2 illustra una seconda realizzazione.

La Fig.3 illustra una terza realizzazione.

La Fig. 4 illustra una quarta realizzazione.

Descrizione di modi preferiti di realizzare l'invenzione

La Fig. 1 mostra un processo secondo un modo di realizzare l'invenzione basato su pre-reformer e reformer autotermico ATR ad ossigeno.

I blocchi di Fig. 1 denotano i seguenti sistemi o apparecchi:

AUX	forno preriscaldatore della carica e caldaia ausiliaria (auxiliary boiler)
PRE	pre-reformer
ATR	reformer autotermico
POX	reattore di ossidazione parziale
SHF	sezione di shift
CDR	sezione di rimozione CO2 (decarbonatazione)
MET	metanatore
SYN	sezione di sintesi
HRU	sezione di recupero idrogeno
ASU	sezione di separazione (frazionamento) aria

Una carica 10 comprendente gas naturale e vapore è preriscaldata in AUX e convertita in un gas di sintesi 11 attraverso i reformer PRE e ATR. Il reformer autotermico ATR opera con una corrente 22 di aria arricchita o di ossigeno.

Il gas di sintesi 11, contenente H2, CO e CO2, è sottoposto a reazione di shift in SHF e successivamente a rimozione di CO2 in CDR. La sezione SHF può comprendere trattamenti di shift a diversa temperatura. La sezione CDR per esempio opera con lavaggio chimico-fisico del gas con soluzione acquosa di ammine.

La sezione CDR produce un gas di sintesi 12 a ridotto contenuto di CO2 e una corrente 13 di CO2 che può essere sequestrata o utilizzata per altri scopi di processo, ad esempio per produrre urea.

Preferibilmente il gas di sintesi 12 ha la seguente composizione: 98% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

Una parte 14 di detto gas di sintesi 12 a ridotto contenuto di CO2 è utilizzata come combustibile in un forno nel front-end, per esempio in un riscaldatore della carica (blocco AUX). La restante parte 18 di gas di sintesi è ulteriormente trattata nel metanatore MET.

Nell'esempio la quota fuel 14 di gas di sintesi, insieme a un gas di coda 15 della sezione HRU, alimenta uno o più utilizzatori del blocco AUX attraverso la linea fuel 16. Opzionalmente una quantità opportuna di gas naturale 17 (trim fuel) è aggiunta al gas 16.

La quota processo 18 del gas di sintesi, dopo passaggio nel metanatore (opzionale), è addizionata con azoto 19 proveniente dalla sezione di separazione aria ASU.

Il gas così ottenuto, insieme a una corrente di idrogeno 20 recuperata dalla sezione HRU, alimenta la sezione di sintesi SYN. Detta sezione di sintesi produce ammoniaca 23 e una corrente 21 di gas di spurgo trattato nella sezione HRU per il recupero dell'idrogeno in essa contenuto.

La sezione di separazione ASU produce, oltre all'azoto 19, anche la corrente 22 di aria arricchita o di ossigeno per il reformer autotermico ATR.

La Fig. 2 mostra un processo secondo un modo preferito di realizzare l'invenzione basato su reforming primario e ATR.

Il blocco SMR di Fig. 2 denota il reformer primario (o steam reformer) più ausiliari, ad es. generatori di vapore. I restanti simboli di Fig. 2 corrispondono ai simboli di Fig. 1 e pertanto la descrizione non è ripetuta.

In Fig. 2 è mostrata anche una linea opzionale 15a per riciclare parte del gas di coda 15 dalla unità HRU all'alimentazione del reformer primario SMR.

La Fig. 3 mostra un processo basato su ATR, simile a Fig. 1, ma comprendente una purificazione della quota di processo del gas di sintesi in una sezione PUR, che in questo esempio comprende una unità PSA.

La quota fuel 14 separata dal gas di sintesi 12 a ridotto contenuto di CO2 è suddivisa in una prima porzione 14a utilizzata come combustibile in un forno nel front-end, per esempio nel blocco AUX, e una seconda porzione 14b esportata come fuel in eccesso. La restante parte 18 di gas di sintesi è ulteriormente trattata nell'unità PSA.

Una porzione 23 dell'effluente dell'unità PSA è (opzionalmente) esportata come fuel in eccesso. Detta porzione 23 ha una maggiore purezza in idrogeno rispetto alla porzione di gas 14b.

Nell'esempio di Fig. 3, la porzione 14a di gas di sintesi separato come quota fuel, insieme a un gas di scarto (tail gas) 25 dell'unità PSA, alimenta uno o più utilizzatori del blocco AUX attraverso la linea fuel 26.

La Fig. 4 mostra un processo basato su POX, comprendente una purificazione della quota di processo del gas di sintesi in una sezione PUR comprendente dryer e liquid nitrogen wash (LNW).

Similmente alla forma di realizzazione di Fig. 3, anche in questo caso la quota fuel 14 separata dal gas di sintesi 12 a ridotto contenuto di CO2 è suddivisa in una prima porzione 14a utilizzata come combustibile per esempio nel blocco AUX ed una seconda porzione 14b esportata come fuel in eccesso. Detta porzione 14a, insieme a un gas di scarto (tail gas) 35 della sezione PUR, alimenta uno o più utilizzatori del blocco AUX attraverso la linea fuel 36. Detto gas di scarto 35 risulta dalla combinazione del gas di scarto del LNW e del dryer.

Il processo dell'invenzione consente di produrre ammoniaca con emissioni di CO2 pari a circa 0.1 t/t contro circa 0.7 t/t dell'arte nota.

Tutti gli schemi illustrati possono essere il risultato dell'ammodernamento di un impianto ammoniaca con reformer secondario ad aria.

In una realizzazione, la procedura di ammodernamento comprende essenzialmente i seguenti passi:

installare l'unità ASU per generare la corrente 22 di ossigeno o aria arricchita;

modificare il reformer secondario per accettare detta corrente 22 invece di aria;

aumentare la quota di gas naturale destinato al processo e ridurre la quota di gas naturale destinato a fuel;

rivampare la esistente sezione di desolforazione del gas naturale per aumentarne la capacità in ragione della maggiore portata di gas di processo;

rivampare la esistente sezione CDR per aumentarne la capacità in ragione della maggiore quantità di CO2 da separare.

Si comprende che l'ammodernamento non richiede di fare costose modifiche al reformer, agli scambiatori e tubazioni del frontend, alla sezione di shift. Ciò è dovuto al fatto che la portata volumetrica di gas attraverso il front-end non aumenta nonostante la generazione della quota aggiuntiva di gas (quota fuel).

Esempio

La tabella 1 seguente si riferisce a un impianto con capacità di 3000 ton metriche per giorno (MTD) di ammoniaca prodotta.

La tabella 1 confronta le seguenti opzioni:

(1): impianto dell'arte nota con reformer primario e reformer secondario alimentato ad aria.

(2): impianto dell'arte nota, come da opzione (1), con cattura del CO2 dai fumi del reformer primario.

(3): impianto secondo l'invenzione, come da Fig. 1.

(4): impianto secondo l'invenzione, come da Fig. 2.

Tabella 1

Case		(1) Arte nota	(2) Arte nota	(3) Inv.	(4) Inv.
NH3 production	MTD	3000	3000	3000	3000
Net Natural Gas consumption based on gas LHV (FEED+FUEL-Steam exported e.g. to urea)	Gcal/t NH3	6.7	7.4	7.0	6.9
	Gcal/t NH3		+0.7	+0.3	+0.2
CO2 captured in process	MTD	3600	3600	5200	5100
CO2 to atmosphere (contained in flue gas)	MTD	2100	200	200	200
CO2 to atmosphere (contained in flue gas)	t/t NH3	0.7	0.1	0.1	0.1
Main Equipment size					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	100	145	140
ASU O2 capacity	%	n/a	n/a	100	60
Portata del frontend (uscita secondario / ATR)	%	100	100	120	97

La tabella mostra che il processo dell'invenzione (opzione 3) richiede un front-end adeguato per produrre anche la quota di gas da usare come combustibile nei forni, infatti la quantità di CO2 catturata nel processo ammonta a 5200 MTD rispetto a 3600 delle opzioni (1) e (2), e la portata di syngas nel frontend è circa il 20% in più di FIG 1 e 2. Nonostante questo il consumo dell'impianto è molto inferiore all'opzione (2) (7.0 invece di 7.4 Gcal/MT) e competitivo con l'impianto senza cattura secondo l'opzione (1). Il duty totale dei forni è solo il 75% del caso (1).

Nel caso (4) il consumo energetico ottenuto è inferiore al caso (3), pari a 6.9 Gcal/MT, ed anche il costo dell'impianto è inferiore. Questo perché nel caso (4) la quantità di CO2 separata nel processo è inferiore rispetto a (3); il duty dei forni è maggiore rispetto a (3) ma è confrontabile con le opzioni (1) e (2); il consumo di ossigeno nettamente inferiore a (3); la portata nel frontend è nettamente inferiore a (3) e confrontabile con (1) e (2).

Gli esempi mostrano come il nuovo processo sia più efficiente e competitivo dell'arte nota.

L'esempio mostra anche il vantaggio di modificare un impianto operante come da opzione (1), preferibilmente implementando l'opzione (4). Infatti, in questa ipotesi il duty dei forni e la portata di gas restano sostanzialmente immutate mentre si abbattono le emissioni di CO2. L'invenzione così raggiunge lo scopo di minimizzare le emissioni di CO2 di un impianto convenzionale senza perdere produzione di ammoniaca.

La tabella 2 seguente si riferisce a un impianto con capacità di 3000 ton metriche per giorno (MTD) di ammoniaca prodotta, autosufficiente dal punto di vista del vapore e dell'energia elettrica. Il processo comprende i consumi relativi alla compressione della CO2 sequestrata fino alla pressione di 100 bar. Per ciascun processo, il consumo di gas naturale e le emissioni di CO2 indicate considerano anche la produzione di vapore surriscaldato in AUX per muovere tutte le turbine, e la produzione dell'energia elettrica necessaria per il processo.

La tabella 2 confronta le seguenti opzioni:

(1) impianto secondo l'invenzione, con SMR+ATR come da Fig. 2, nelle seguenti varianti:

a. con S/C globale = 2.7, shift composto da HTS ed LTS, metanatore, trim fuel con portata corrispondente al 10% del duty richiesto del forno;

b. come 1a, ma senza trim fuel.

(2) impianto secondo l'invenzione, con prereformer+ATR come da Fig. 3, nelle seguenti varianti:

a. con S/C globale = 2, shift composto da MTS ed LTS, PSA, trim fuel con portata corrispondente al 10% del duty richiesto del forno;

b. come 2a, senza trim fuel, con il selectoxo a valle di SHF e monte di CDR per convertire il CO residuo.

(3): impianto secondo l'invenzione, con POX, come da Fig. 4, nelle varianti:

a. con S/C globale = 2, Shift composto da MTS ed LTS, dryer LNW, trim fuel con portata corrispondente al 10% del duty richiesto del forno;

b. come 2a, senza trim fuel, con ossidazione catalitica selettiva di CO (processo Selectoxo™) a valle della reazione di shift e a monte della rimozione di CO2.

Tabella 2

	1a SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
Produzione giornaliera di NH3, MTD	3000	3000	3000	3000	3000	3000
Portata giornaliera di CO2 sequestrata, MTD	5600	5800	5100	5300	5350	5600
Consumo netto di gas naturale (relativo all'esempio 1a), adimensionale	100%	100%	93%	93%	95%	95%
Emissioni di CO2 in atmosfera per unità di ammoniaca prodotta, t CO2/t NH3	0.15	0.075	0.17	0.10	0.15	0.05
Ripartizione delle emissioni di CO2						
- trim fuel	50%	nil	20%	nil	20%	nil
- CH4 slip nel process gas	15%	29%	40%	79%	30%	63%
- CO slip nel process gas	34%	69%	39%	19%	49%	34%
- CO2 slip nel process gas	1%	2%	1%	2%	1%	3%

In Tabella 2:

"Trim fuel" come definito nel brevetto;

"CH4 slip nel process gas" è il contenuto di metano residuo del gas di sintesi prodotto nel frontend (cioè in SMR + ATR nel caso 1, in prereformer + ATR nel caso 2, POX nel caso 3), quantificato a monte dell'eventuale metanazione;

"CO slip nel process gas" è il contenuto di monossido di carbonio residuo del gas di sintesi a valle della sezione di shift;

"CO2 slip nel process gas" è il contenuto di anidride carbonica residua del gas di sintesi a valle della sezione di rimozione della CO2;

La tabella 2 permette di fare numerose osservazioni.

- Nel caso SMR+ATR dell'esempio 1a, il trim fuel è il maggior contribuente alle emissioni di CO2; evitare il trim fuel, adottando il metodo dell'export di surplus fuel dell'invenzione, permette di ridurre notevolmente le emissioni a < 0.1 t/t, come riportato in tabella per l'esempio 1b; contestualmente, la quantità di CO2 sequestrata aumenta da 5600 a 5800 MTD.

- Nel caso SMR+ATR, lo slip di CO nel process gas è il secondo contribuente alle emissioni di CO2 nell'esempio 1a, e diventa il primo nell'esempio 1b; un'eventuale applicazione del selectoxo al caso 1a o 1b ridurrebbe efficacemente le emissioni di CO2; lo slip di CH4 nel process gas elo slip di CO2 nel process gas hanno un contributo alle emissioni di CO2 di minore rilevanza.

- Il consumo energetico globale dei casi basati su ATR e POX + purificazione (2 e 3) è decisamente inferiore rispetto a quello dei casi basati su SMR + ATR (1a ed 1b), ciò è dovuto principalmente alla purificazione del gas di sintesi (che migliora l'efficienza della sezione di sintesi, ed evita lo spugo); la

quantità di CO2 sequestrata in queste opzioni (2a, 3a; oppure 2b, 3b) è conseguentemente inferiore ai casi 1a oppure 1b.

- Le emissioni dovute all'uso del trim fuel nelle opzioni 2a (ATR) e 3a è circa il 20% delle emissioni totali, molto minore del caso 1a, a conferma del fatto che il calore richiesto del forno in queste due opzioni è assai inferiore rispetto all'opzione 1a.

- Nelle realizzazioni con ATR o POX, assumono una rilevanza maggiore il CO e CH4 residui, conseguenza del minore rapporto S/C a cui operano ATR e POX rispetto a SMR+ATR; il POX opera ad una temperatura più elevata di ATR, che determina una minore quantità residua di CH4, ma una maggiore quantità residua di CO.

- In entrambi i casi 2b e 3b, è evidente il miglioramento apportato dall'ossidazione selettiva di CO, per ridurre il CO slip, e dal fatto di evitare il trim fuel.

- Si osserva che sia il POX che l'ATR raggiungono emissioni molto basse, addirittura 0.05 per il POX, 0.1 per l'ATR, confrontabili con SMR+ATR ma con consumi energetici inferiori, pertanto preferibili.

L'esempio dimostra come l'invenzione consenta di raggiungere livelli di emissioni di CO2 estremamente bassi, corrispondenti ad una cattura quasi completa (>98%), pur mantenendo consumi energetici competitivi.

RIVENDICAZIONI

1) Processo di sintesi dell'ammoniaca da gas naturale comprendente:

conversione di una carica di gas naturale desolforato e vapore, con aria arricchita in ossigeno o con ossigeno, in un gas di sintesi (11) contenente idrogeno, CO e CO2, all'interno di una sezione di conversione,

un trattamento di detto gas di sintesi (11) comprendente almeno una reazione di shift del monossido di carbonio in CO2, e successiva separazione di CO2 dal gas, così ottenendo un gas di sintesi (12) a ridotto contenuto di CO2 e una corrente gassosa ricca di CO2, contenente il CO2 separato dal gas;

opzionalmente, una fase di metanazione del gas di sintesi e/o una aggiunta di azoto al gas di sintesi,

caratterizzato da:

separazione di una parte (14) di detto gas di sintesi (12) a ridotto contenuto di CO2 come quota combustibile, in cui detta quota combustibile (14) è alimentata come combustibile a almeno un forno .

2) Processo secondo la rivendicazione 1, in cui detta separazione della quota combustibile comprende la divisione di detta corrente di gas di sintesi a ridotto contenuto di CO2 in almeno una prima corrente e una seconda corrente, dette correnti aventi la medesima composizione, in cui la prima corrente forma la quota combustibile e la seconda corrente rappresenta gas di processo destinato alla sintesi di ammoniaca, eventualmente dopo ulteriore purificazione.

3) Processo secondo la rivendicazione 1 o 2, in cui detta quota combustibile (14) è compresa tra 1% e 40% della quantità totale di detto gas di sintesi (12) a ridotto contenuto di CO2, preferibilmente tra 10% e 30%.

4) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detta quota combustibile è separata a monte della fase di metanazione o a monte della fase di aggiunta di azoto.

5) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detto gas di sintesi (12) a ridotto contenuto di CO2 contiene non più di 1000 ppm in volume di CO2.

6) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detta aria arricchita contiene almeno il 50% di ossigeno, preferibilmente almeno il 90%.

7) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui detta quota combustibile (14) del gas di sintesi alimenta uno o più tra i seguenti apparecchi: un forno per la produzione e/o surriscaldo di vapore; uno o più bruciatori di un reformer primario a vapore; uno o più forni di pre-riscaldo della carica di un reformer autotermico o di un reattore a ossidazione parziale o di una sezione di desolforazione del gas naturale.

8) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui: un gas di spurgo (21) del processo di sintesi dell'ammoniaca, contenente idrogeno e metano, è trattato per recuperare l'idrogeno in esso contenuto, con ottenimento di un gas ricco di idrogeno (20) e di un gas di coda (15) contenente metano; almeno parte (15a) di detto gas di coda (15) è riciclata come gas di processo e sottoposta alla detta fase di conversione del gas naturale in gas di sintesi.

9) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui: una parte del detto gas di sintesi (12) a ridotto contenuto di CO2 è trattata in un'unità per separare azoto ottenendo una prima corrente di gas di sintesi a ridotto contenuto di azoto e una seconda corrente ricca di azoto; almeno una parte di detta prima corrente, preferibilmente tutta, è utilizzata come combustibile; la eventuale restante parte di detta prima corrente è alimentata alla sintesi dell'ammoniaca insieme alla seconda corrente.

10) Processo secondo una qualsiasi delle rivendicazioni precedenti comprendente anche una fase di espansione, con produzione di lavoro meccanico, del gas di sintesi (12) a ridotto contenuto di CO2, opzionalmente dopo averlo scaldato.

11) Processo secondo una qualsiasi delle rivendicazioni precedenti in cui il rapporto vapore/carbonio globale nella fase di conversione è maggiore di 2.0, preferibilmente maggiore di 2.4 e più preferibilmente maggiore di 2.7.

12) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui:

detta quota fuel (14) di gas di sintesi costituisce tutto il combustibile dei forni utilizzati nella sezione di conversione, o

è presente una quantità di gas naturale come combustibile di regolazione (trim fuel), il contributo di detto combustibile di regolazione al calore di combustione totale essendo non superiore al 15%.

13) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui:

la quota fuel è prodotta in quantità in eccesso rispetto al combustibile necessario per la sezione di conversione, la quantità di detta quota fuel eccedente la richiesta essendo esportata dal processo, e

la regolazione della sezione di conversione è operata modulando la quantità di detta quota fuel diretta alla sezione di conversione e la quantità esportata dal processo.

14) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui:

la conversione della carica di gas naturale in gas di sintesi comprende una fase di reforming autotermico, opzionalmente con pre-reforming, o una fase di ossidazione parziale;

detta fase di reforming autotermico o ossidazione parziale è condotta con rapporto vapore/carbonio non superiore a 2.

15) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui la conversione del gas naturale in gas di sintesi comprende: un reforming primario del gas naturale in presenza di vapore e un reforming secondario effettuato con detta corrente di ossigeno o aria arricchita.

16) Processo secondo una qualsiasi delle rivendicazioni precedenti, in cui le emissioni di CO2 sono inferiori a 0.5 ton di CO2 emessa per ton di ammoniaca prodotta.

17) Metodo di ammodernamento di un impianto per la sintesi dell'ammoniaca da gas naturale o impianto ammoniaca-urea, in cui:

l'impianto comprende una sezione di reforming che include un reformer primario con vapore e reformer secondario ad aria, e una sezione di trattamento del gas di sintesi tramite shift di monossido di carbonio in diossido di carbonio, decarbonatazione e eventualmente metanazione,

e il metodo di ammodernamento comprende almeno:

fornire una corrente (22) di aria arricchita o di ossigeno e utilizzare detta corrente quale ossidante, al posto dell'aria, per il reformer secondario;

separare una quota parte (14) del gas di sintesi, a valle della decarbonatazione, per utilizzo come quota combustibile, e destinare una restante quota di processo del gas di sintesi alla conversione in ammoniaca.

alimentare detta quota combustibile (14) del gas, avente un ridotto contenuto di CO2, come combustibile per almeno un forno dell'impianto.

18) Metodo di ammodernamento secondo la rivendicazione 17 comprendente: installare una unità di separazione aria per fornire detta corrente di aria arricchita o di ossigeno, in cui detta unità di separazione fronisce anche una corrente di azoto che viene aggiunta alla quota di processo del gas di sintesi per ottenere il desiderato rapporto tra H2 e N2.

RIASSUNTO

Processo di sintesi dell'ammoniaca da gas naturale comprendente conversione di una carica di gas naturale desolforato e vapore, con aria arricchita in ossigeno o con ossigeno, in un gas di sintesi (11), e trattamento del gas di sintesi (11) con shift e decarbonatazione, in cui una parte del gas di sintesi a ridotto contenuto di CO2, ottenuto dopo decarbonatazione, è separata e utilizzata come quota combustibile per uno o più forni della sezione di conversione, e la restante parte del gas è utilizzata per produrre ammoniaca.

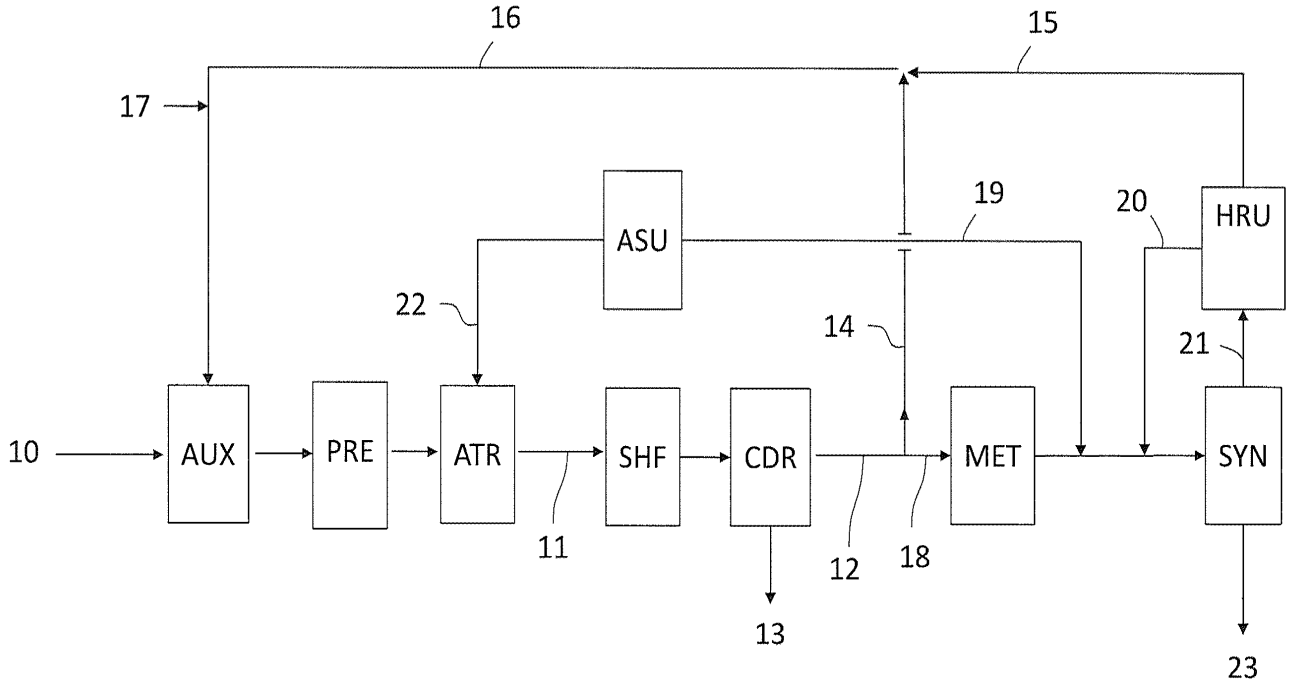

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FIG. 1

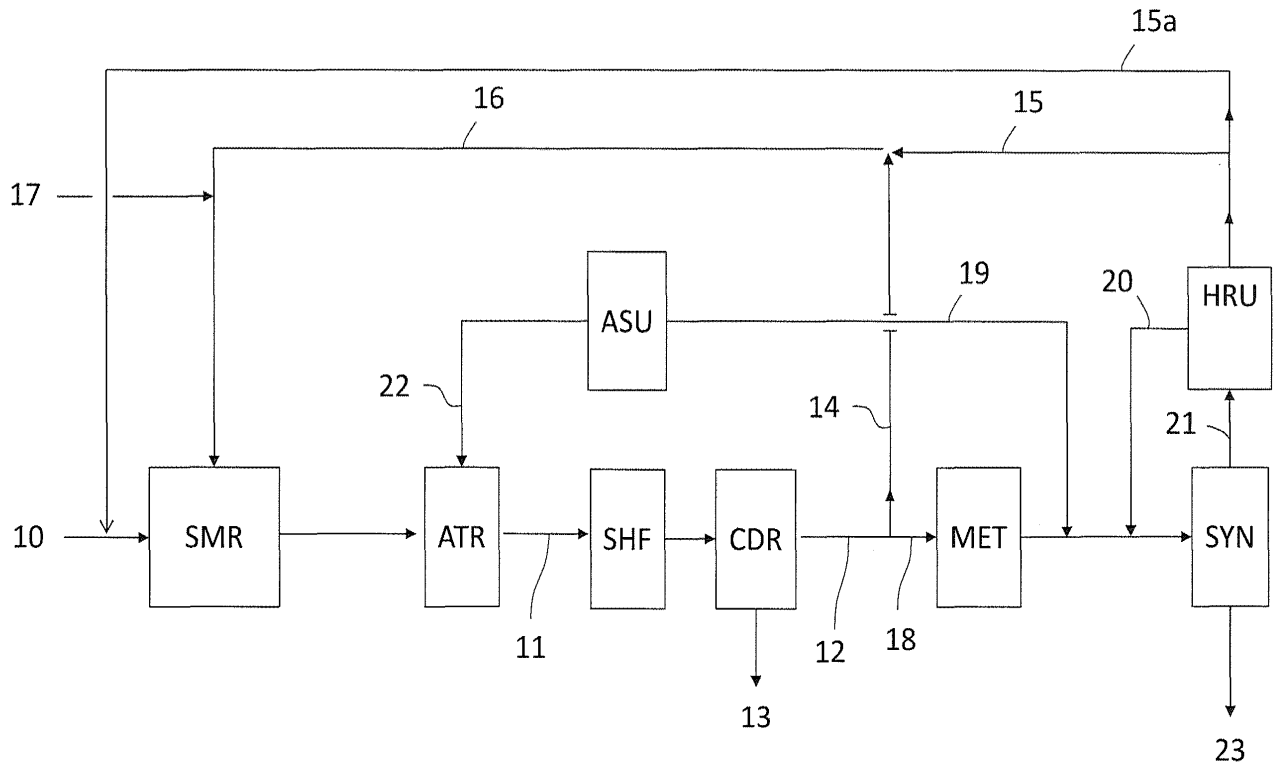

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FIG. 2

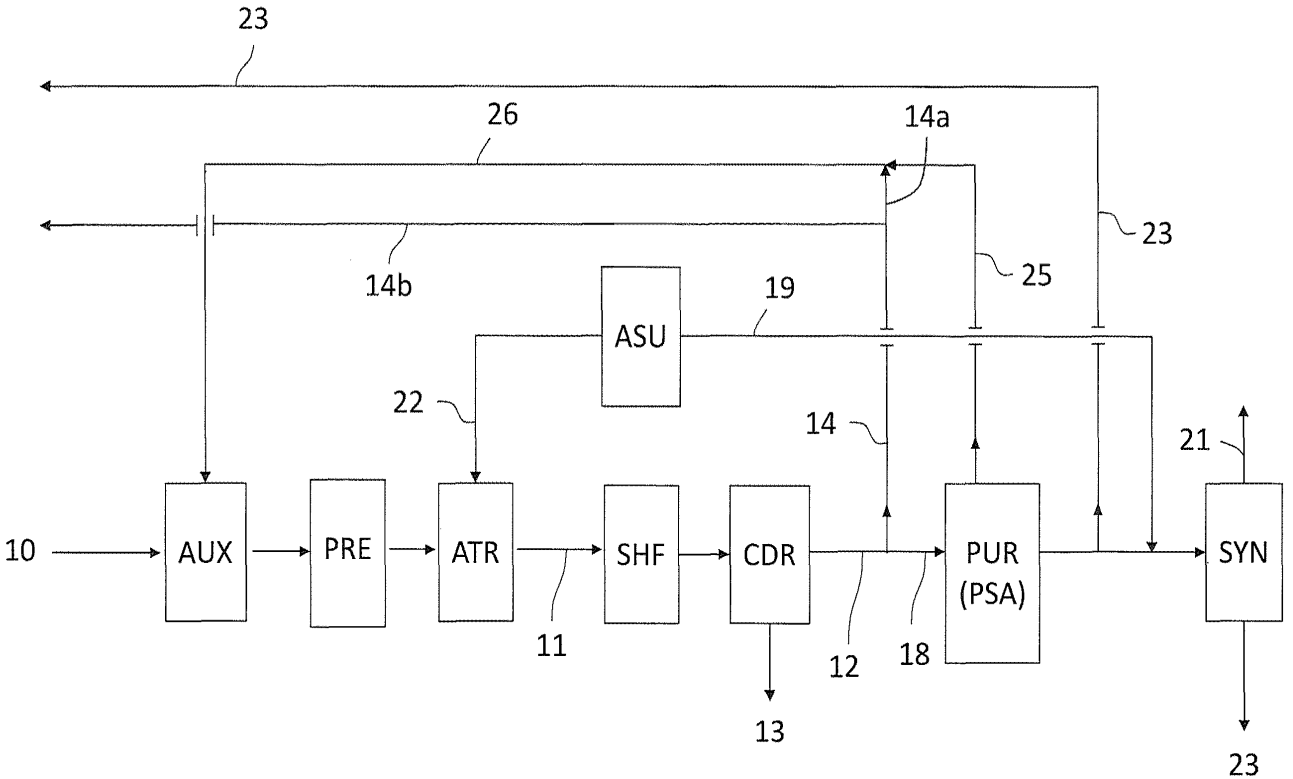

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FIG. 3

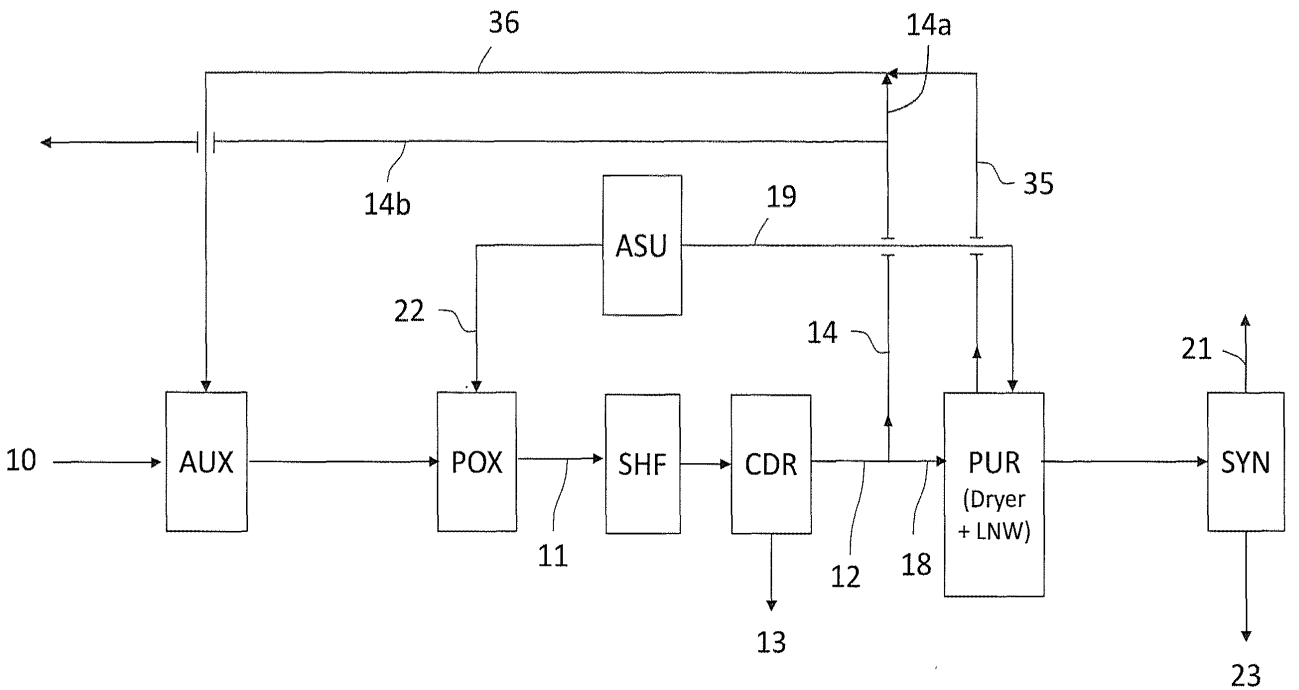

36
14a
14b
35
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ASU
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(Dryer
+ LNW)
SYN
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FIG. 4

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Process for the synthesis of ammonia with low emissions of CO2 in atmosphere

Field of application

The invention relates to the field of ammonia synthesis plants fed with natural gas (NG).

Prior art

The ammonia synthesis plants of the type considered here comprise a section adapted to convert the natural gas into a make-up gas containing hydrogen and nitrogen, and a synthesis section wherein said make-up gas reacts catalytically at high pressure to produce ammonia.

The section which generates said make-up gas is referred to in the technical language as the "front end". The term "back end" is instead used to denote the section for ammonia synthesis and the respective cooling section intended to cool the effluent of the synthesis section in order to separate the ammonia.

In the front end, the desulphurized natural gas undergoes reforming, resulting in a gas containing essentially hydrogen, carbon monoxide CO and carbon dioxide CO2. Said gas then undergoes a shift reaction which converts CO into CO2; removal of CO2 (decarbonation) and preferably methanation.

The reforming process, in a common type of plant, comprises primary steam reforming and a subsequent catalytic air-fired secondary reforming. The primary reformer is heated by burners fuelled by a part of the available natural gas. In the secondary reformer the effluent from the primary reformer burns due to contact with the oxygen contained in the air. In some plants other reforming configurations are used, for example an autothermal reformer (ATR) preceded by a furnace for heating the charge, i.e. the gaseous mixture fed to

said reformer.

The above described ammonia plants result in significant emissions of CO2 into the atmosphere, overall in the region of 100 million tonnes of CO2 per year. One of the main sources of CO2 emission consists in the combustion fumes of the primary reformer and other burner furnaces if any, for example auxiliary heaters.

For environmental reasons, it is required to minimize the CO2 emissions from the fumes of the NH3 plants. The problem affects in particular the older ammonia plants which are less efficient than the new ones and have greater CO2 flue emissions in relation to the quantity of ammonia produced. It is also necessary that the reduction of the emissions should not increase excessively the costs for production of the ammonia.

According to the present state of the art, the processes for capturing CO2 from fumes are based on washing with solvents (for example the solvent KS-1™ produced by Mitsubishi). The associated plants are, however, costly and complicated, have a high energy consumption and require expensive solvent. Therefore these CO2 capturing processes cannot be applied to the plants considered here since they would increase excessively the costs for production of the ammonia.

In some ammonia synthesis processes of the prior art, part of the fuel may be supplied by a purge flow obtained, for example, from a cryogenic purification section of the synthesis gases or from a PSA unit. Said purge flow may have a reduced CO2 content. However, said purge flow accounts for a small amount of the total fuel and does not solve the problem of the CO2 emissions in the atmosphere.

Summary of the invention

The object of the invention is to provide a method for conducting ammonia synthesis processes with CO2 emissions into the atmosphere which are

greatly reduced compared to the prior art. Another object of the invention is to provide a method for revamping the existing plants, of the type using air-fed secondary reformers able to reduce drastically the CO2 emissions into the atmosphere.

The objects are achieved with a process and a revamping method according to the claims.

According to the invention, a process for synthesis of ammonia from natural gas comprises:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, to form a synthesis gas containing hydrogen, CO and CO2;

a treatment of said synthesis gas comprising at least one shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas, obtaining a make-up gas containing nitrogen and hydrogen in a suitable molar ratio for ammonia synthesis,

characterized by:

separation of a part of said CO2-depleted synthesis gas, obtaining a fuel fraction of the synthesis gas, wherein said fuel fraction is fed as fuel to at least one furnace.

The invention also relates to a method for revamping a plant originally comprising a reforming section which includes a primary steam reformer and air-fired secondary reformer, and treatment of the synthesis gas comprising a shift reaction of carbon monoxide into carbon dioxide, decarbonation and

optionally methanation. The revamping method comprises at least:

providing a flow of enriched air or oxygen and using said flow as an oxidant for the secondary reformer instead of the air;

separating a part of the synthesis gas downstream of decarbonation,

feeding said part of the synthesis gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

The term "furnace" is understood as meaning an apparatus chosen from among: a steam reformer or a charge preheater or a steam generator or a steam superheater. These apparatus, which operate by means of combustion, are identified by the term "fired heater". Said furnace in some embodiments forms part of the section for converting the natural gas into synthesis gas. In combined ammonia/urea plants said furnace may form part of the urea section.

The portion of synthesis gas which is separated and sent to said at least one furnace is termed fuel fraction of the gas available after the shift step. Preferably, said fuel fraction is comprised between 1% and 40% of the available gas, more preferably between 10% and 30% and even more preferably between 20% and 30%. For example in a preferred embodiment the fuel fraction is equal to 30%. The remaining part, which is intended to be converted into ammonia, is called process fraction.

It should be noted that said fuel fraction is relatively high, for example about 1/3 of the total. The invention in fact envisages that a non-negligible portion of synthesis gas is allocated to fuel in order to reduce the CO2 emissions. This results in the need to produce an additional quantity of synthesis gas, but, as will be explained more clearly below with the aid of the examples, this necessity is compensated for by the advantages of the invention.

The separation of the fuel fraction is advantageously performed by splitting a

process flow, for example a process gas after shift and decarbonation. As a result of said splitting, the fuel fraction and the remaining part of the gas, also called process fraction, have the same composition.

It should be noted that the present invention envisages deliberately allocating a part of the process flow to the fuel fraction, the fuel fraction being directly separated from the process flow and having the same composition. The prior art, on the other hand, teaches only allocating as fuel any purge streams derived from purification processes and containing methane. The said synthesis gas with a low CO2 content (CO2-depleted syngas) preferably contains no more than 1000 ppm by volume (0.1%) of CO2. Said gas is composed essentially of hydrogen ((H2) with any small residual quantities of CO and CH4, typically less than 2% by volume and preferably less than 1%.

The combustion of said gas is substantially free from production of CO2. In fact, the combustion of the hydrogen does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The invention suggests using a process gas part as fuel for one or more furnaces of the reforming section, differently from the prior art which, for this purpose, uses part of the natural gas, i.e. a hydrocarbon. The process gas part (fuel fraction) is suitably separated after a CO2 removal treatment and, as explained further above, it contains essentially hydrogen which may burn without forming CO2. Consequently it can be understood that the invention allows the CO2 emissions into the atmosphere to be drastically reduced.

Said oxygen-enriched air preferably contains at least 50% oxygen by volume and more preferably at least 90% oxygen by volume and even more preferably at least 95%. The advantages of a high oxygen content in the enriched air are as follows: greater calorific power of the synthesis gas; smaller flow of flue discharge gas; smaller volumetric flow through the apparatus of the conversion section and, consequently, smaller apparatus.

The CO2-depleted synthesis gas preferably forms all - or substantially all - the fuel of the furnaces used for the process. In some embodiments, however, it is preferred to keep a small amount of natural gas which is called "trim fuel" of the furnace. Preferably said small quantity accounts for not more than 15%, more preferably not more than 10%, of the total combustion heat (duty) of the furnace. The trim fuel allows the furnace to be rapidly controlled, for example in order to quickly raise or lower the load if needed.

Said percentage of the combustion heat may be expressed as the product between the flowrate (kg/s or mol/s) and the calorific power (J/kg or J/mol).

According to some embodiments of the invention, methanation of the synthesis gas is performed downstream of decarbonation. The methanation step converts residual CO and CO2 into CH4, consuming H2, in accordance with the reactions CO + 3H2 → CH4 + H2O e CO2 + 4H2 → CH4 + 2H2O.

Preferably, the separation of the fuel fraction from the CO2-depleted synthesis gas is performed before (upstream of) of said methanation step.

The advantage of separating the fuel fraction before methanation is that of not oversizing the methanation section of the fuel fraction, and of not losing the methanation heat of the fuel fraction. Moreover, for the same furnace heat requirement and the same gas temperature, the fuel fraction is slightly less if removed before methanation.

There are no disadvantages as regards CO2 emissions into atmosphere, which are the same by using as fuel both the gas upstream of the methanator and the gas downstream of the methanator, for the same flowrate. In case of nitrogen addition, the fuel fraction is separated before adding nitrogen. The advantage is a greater calorific power of the synthesis gas used as fuel, which does not contain nitrogen, or contains a smaller amount thereof.

After separating the fuel fraction, the CO2-depleted synthesis gas may be optionally treated in a purification section comprising, for example, a PSA unit

or comprising a dryer followed by a cryogenic unit.

The purification section produces at least one stream of ammonia synthesis gas with a reduced content of inerts, and at least one waste stream containing CO, and CH4. The waste stream may also contain H2 and N2. In some embodiments, at least part of the waste gas of said purification section is used as fuel together with the fuel fraction. Consequently, the fuel fraction may be reduced.

The advantage of the purification unit is that of reducing the inerts content in the make-up gas, resulting in known advantages for the ammonia synthesis, including smaller consumption for circulation and a reduction (or even elimination) of the purge flow of the ammonia synthesis loop.

According to the invention, the fuel fraction is advantageously separated upstream of the purification unit. Consequently, only the synthesis gas portion supplied to the ammonia synthesis undergoes treatment in the purification section which, without having to process the synthesis gas corresponding to the fuel fraction, may be realized with much smaller dimensions. The advantage of separating the fuel fraction upstream of the purification unit is that of avoiding oversizing of the purification unit and the corresponding consumption for the fuel fraction of the synthesis gas. Another advantage is the possibility of controlling separately the fuel fraction and the purification unit.

There is no disadvantage in separating the fuel fraction upstream of the purification from the point of view of the CO2 emissions into atmosphere, since the CO, CO2 and CH4 contained in the synthesis gas of the fuel fraction would be separated by the purification unit to form the waste stream and used as fuel.

Advantageously, the purification unit does not need to have an excessively high hydrogen recovery, because the hydrogen "lost" in the waste gas is used

as fuel and does not produce CO2 emissions into atmosphere. The fuel fraction of the synthesis gas is consequently regulated.

Preferably, however, the purification unit has a sufficiently high hydrogen recovery such that the fuel fraction accounts for at least 30%, preferably at least 40%, even more preferably at least 50% of the furnace duty. The applicant has found that this condition is advantageous for the control of the furnace itself independently of the control of the purification unit.

The purification section may comprise selective adsorption of the undesirable components onto a solid. In some embodiments said purification section comprises a PSA (pressure swing adsorption) unit which uses molecular sieves for separating CO, CH4, Ar, H2O and residual CO2. In other embodiments said section comprises at least one dryer for separating residual CO2 and water, followed by a cryogenic unit for separation of CO, CH4 and Ar. The cryogenic separation unit is preferably a Liquid Nitrogen Wash (LNW) unit.

A PSA unit typically produces a single flow of purified product, substantially at the feed pressure, and a single stream of waste gas, at a pressure much lower than the feed pressure. Said waste stream contains CO, CH4, Ar, H2O and residual CO2, and may contain H2 and N2.

If the purification section comprises dryer and LNW, the purified product may emerge as one or more streams, and may already contain H2 and N2 in a suitable ratio for the synthesis of ammonia.

The dryer has a tail gas, product of regeneration of the molecular sieves used for capturing mainly H2O and the traces of residual CO2 contained in the feed, which would freeze during the cryogenic treatment in the LNW unit. The dryer may be regenerated with a nitrogen flow (from the air separation unit). In this case the tail gas containing N2, H2O and CO2 may be discharged into atmosphere or combined with the tail gas of the LNW described below.

The LNW also has at least one tail gas which contains the bottom end product of the LNW absorption column, containing CH4 and CO, in addition to N2 and H2. The discharge gas of the LNW may be conveyed away as fuel.

The tail gas of the LNW may be used at least partly for the regeneration of the dryer before being conveyed away as fuel.

The synthesis gas with a low content of inerts may be conveyed away for ammonia synthesis.

Methanation is an exothermic reaction, but there is not a substantially large amount of reaction heat and it is usually not recovered.

Methanation therefore leaves a small quantity of methane in the synthesis gas (methane slip). The presence of said small quantities of methane in the synthesis gas is not a problem for the purposes of ammonia production, since methane is inert to the synthesis reaction. Methane accumulates in the purge flow of the synthesis loop. However, by using the purge flow of the synthesis loop as fuel, the methane contained therein constitutes a source of CO2, albeit of small entity.

The carbon monoxide contained in the synthesis gas also constitutes a source of CO2, albeit of small entity, both owing to combustion of the synthesis gas used as fuel, and owing to combustion of the waste gas of a purification unit, where present.

In some embodiments of the invention, in order to reduce also this source of CO2 (i.e. the emissions caused by the presence of residual carbon monoxide of the synthesis gas), the process comprises a catalytic purification which selectively converts the CO into CO2 upstream of decarbonation. Selective conversion of the carbon monoxide may be obtained, for example, using the process known as Selectoxo™ which operates with the reaction CO + 1/2 O2 → CO2. The oxygen for selective oxidation of the CO may be a part of the mentioned enriched-air or oxygen flow.

An advantage of said selective conversion of CO into CO2 is that at least part of the residual CO from the shift is converted into CO2 and removed during decarbonation. Consequently, the combustion of the synthesis gas, of the synthesis loop purge flow, or of the purification waste gas, produces a smaller quantity of CO2.

According to the invention, the CO2 flue emissions are mainly determined by the CO, CO2 and CH4 content of the synthesis gas downstream of decarbonation, as well as by the optional trim fuel flow which will be described below.

The combustion of said gas is substantially free from CO2 production. In fact, the hydrogen combustion does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The CO2 production is also derived from the combustion of the methane contained in the synthesis loop purge flow.

In case a purification unit is present, CO2 production is also derived from the combustion of CO, CH4 and residual CO2 of the discharge gas.

According to one aspect of the invention, the fuel fraction is produced in excess compared to the fuel required for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and the regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported by the process.

The conversion of the natural gas into synthesis gas may be performed using different techniques.

According to some embodiments of the invention, the step of natural gas conversion into synthesis gas comprises primary reforming followed by secondary reforming. In some embodiments, more preferably, the conversion

step comprises a catalytic autothermal reforming (ATR), optionally preceded by a preliminary reforming (pre-reforming). An ATR without preliminary reforming is also called "pure ATR". Advantageously, in these embodiments, at least a part of the synthesis gas fuel fraction feeds a furnace for pre-heating the gas prior to autothermal reforming.

The advantage of using ATR, pure or in combination with a pre-reformer, consists in the smaller heat requirement of the furnace compared to the combination of the ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the ATR feed and of the optional pre-reformer according to the invention is suitably chosen at a value not greater than 650°C, lower than the output temperature of the primary reformer, and due to the fact that, in the preheating furnace, there is no progression of the steam reforming reaction (which is endothermic).

A pure ATR, or ATR in combination with a pre-reformer, may advantageously operate with a steam/carbon (S/C) ratio less than that of a primary reformer. Preferably, said S/C ratio is not greater than 2, more preferably not greater than 1.5, even more preferably not greater than 1. This also helps reduce the heat required by the furnace for preheating the feed of the ATR and optional pre-reformer.

In the case of ATR without primary reformer, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

In some embodiments the step for converting the natural gas into synthesis gas comprises a non-catalytic POX (partial oxidation) step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds a furnace for preheating the gas before said partial non-catalytic oxidation or for steam generation or steam superheating.

The advantage of using a POX consists in the smaller heat requirement of the furnace compared to the combination of an ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the POX feed according to the invention is suitably chosen at a value not higher than 500°C, markedly lower than the output temperature of the primary reformer, and due to the fact that in the preheating furnace there is no progression of the steam reforming reaction (which is endothermic). Moreover, POX may advantageously use a S/C ratio lower than that of a primary reformer, preferably not greater than 2, more preferably not greater than 1, even more preferably not greater than 0.5. This also helps reduce the heat required by the preheating furnace.

In the case of POX, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

The reduction in the heat required by the preheating furnace for a POX and for a pure ATR compared to an ATR in combination with a primary reformer provides the following advantages: the fuel fraction of the synthesis gas is less, and it is possible to reduce the quantity of trim fuel, therefore lower CO2 flue emissions may be obtained.

Both in the case of POX with optional purification unit of the synthesis gas and in the case of ATR without primary reformer and with optional purification unit of the synthesis gas, it is preferable to select a purification unit with high hydrogen recovery, for example a liquid nitrogen wash, so as to ensure that the fuel fraction of the synthesis gas is sufficiently large to control the furnace independently of control of the purification unit.

Another advantage of the POX and ATR without primary reformer, consequence of both the smaller fuel fraction and the smaller steam/carbon ratio, is the smaller autogenous steam production, which reduces the heat

required for the associated overheating, the fuel fraction, the CO2 flue emissions and the total natural gas consumption.

The smaller autogenous steam production may result in a lack of steam for driving the turbines or of electricity for powering the motors of the machines. The missing energy may be conveniently imported from outside the plant as electricity with reduced CO2 emissions, for example generated by renewable sources. It should be pointed out that this synergy is not possible if the process already produces an excess of steam or energy, for example in the case of combination of primary reformer and ATR with a fairly large fuel fraction.

In some embodiments the step of converting the natural gas into synthesis gas also comprises a steam reforming step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds the burners of the reformer.

A part of the fuel fraction may be allocated, in some embodiments, to furnaces for the production and/or superheating of steam.

The invention also allows to produce the electricity necessary for the synthesis of ammonia or of its derivatives (for example urea) with low emissions of CO2, using as fuel CO2-depleted synthesis gas, for example in the following ways:

- expansion in a turbo generator of a flow of steam produced in a steam generator or steam superheater, fed by the CO2-depleted synthesis gas as fuel;

- combustion in a gas turbine or in a gas engine, fed by the CO2-depleted synthesis gas as fuel.

Generally, in ammonia processes, a purging gas is extracted from the ammonia synthesis loop, in order to remove the inert substances from the synthesis loop, and said purging gas is treated with a process for recovery of

the hydrogen contained in it (HRU). Said recovery process generates a hydrogen-rich gas which may be reused for synthesis and a tail gas containing most of the methane initially contained in the purging gas. The methane in the tail gas is practically all that contained in the process fraction of the synthesis gas. Normally said tail gas, given its relatively high methane content, is used exclusively as fuel. This use of tail gas, however, generates CO2 emissions.

According to one aspect of the invention at least a part of said tail gas is recycled as process gas during the natural gas conversion step, for example during the reforming or partial oxidation step. An associated advantage is a further reduction in the CO2 emissions.

In some embodiments a part of the said CO2-depleted synthesis gas is treated in a nitrogen (N2) separation unit, preferably a membrane unit, obtaining a nitrogen-depleted synthesis gas and a nitrogen-rich flow; at least a part of the nitrogen-depleted synthesis gas (preferably all of it) is used as fuel; the remaining part is fed to the ammonia synthesis together with the nitrogen-rich flow.

This configuration is particularly advantageous if the O2-enriched air does not have a very high purity (for example less than 95% of O2) and/or if the natural gas contains nitrogen. Three benefits are obtained: an increase in the calorific power of the fuel gas, a reduction in the flow of combustion fumes (and the power of the respective ID fan) and conservation of the nitrogen which is a reagent for the ammonia. The membrane nitrogen separation unit is further preferred because said unit may operate using the pressure difference between the synthesis gas (produced at high pressure) and the combustion in the furnace (which occurs at atmospheric pressure). Moreover, the nitrogen-rich flow, which is used for synthesis, does not lose pressure.

The configuration described above, which envisages separation of the nitrogen from the synthesis gas, is applicable also in a conventional process, with primary steam reformer and secondary air-fired reformer, resulting in the

advantage that it is not required to modify or enlarge the air compressor. However, with a secondary air-fired reformer and without modifying the compressor, and therefore without being able to increase the air flow, the additional fraction of synthesis gas (required as fuel) would have to be produced by increasing the capacity of the primary reformer and/or installing a gas-heated reformer (GHR), both solutions being very costly. For these reasons, the nitrogen separation described is particularly preferred in combination with the use of the enriched air during conversion of the natural gas into synthesis gas.

In some embodiments, it is envisaged expanding, with production of mechanical work, the CO2-depleted synthesis gas after optionally heating it.

Said gas is available at a pressure higher than the pressure required for combustion in a furnace and therefore it may be expanded in a suitable machine, such as an expander or a turbine, producing mechanical work. For example, said expansion may be from about 25 bar to about 3 bar. The gas has a high specific volume given that it comprises essentially H2 and for this reason its expansion may generate a considerable amount of power. The power obtained may cover partly the process requirements, making it more efficient.

In some embodiments the shift step comprises two steps at different temperatures, for example preferably one high-temperature shift (HTS), for example carried out using an iron-based catalyst, followed by a low-temperature shift (LTS) or medium-temperature shift (MTS), for example carried out using a copper-based catalyst. The associated advantage is that of obtaining the maximum conversion of the CO into CO2, which will then be separated during the decarbonation step, so as to obtain the minimum residual CO content in the synthesis gas used as fuel. Since the CO is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In some embodiments, in which a relatively low overall S/C ratio is used, for example <2.7, the shift preferably comprises two steps in series carried out over catalyst suitable to operate with a low steam content, for example a copper-based catalyst. In this configuration, the first step consists of a medium temperature shift (MTS), which is preferably pseudo-isothermal and operates in the temperature range of 200-320°C, and the second step is a low temperature shift (LTS) operating in the temperature range 180-250°C.

The conversion of the natural gas into synthesis gas, for example by means of reforming, is preferably performed at a pressure lower than 50 bar, more preferably lower than 40 bar, and even more preferably lower than 30 bar.

Generally the prior art teaches the preference for high conversion pressures, in order to increase the capacity of the conversion section (front end) and reduce the consumption of synthesis gas compression. The present invention is instead preferably implemented with low conversion pressures in order to obtain the maximum conversion of the methane, since the steam reforming reaction is favoured at a lower pressure, so as to have the minimum residual methane content in the synthesis gas used as fuel. Since the methane is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of ATR, a high methane conversion is also obtained by operating at a relatively high output temperature, >950°C, preferably >1000°C, even more preferably > 1030°C.

In the case of POX, a high methane conversion is also obtained by operating at a relatively high output temperature, >1200°C, preferably >1300°C.

In some embodiments the overall steam/carbon (S/C) ratio during conversion is greater than 2.0, preferably greater than 2.2 and more preferably greater than 2.7. Generally the prior art teaches a preference for low S/C ratios in order to increase the capacity of the conversion section (front end). The

invention instead envisages a relatively high S/C ratio in order to maximize the conversion of the methane and the CO during the shift step and reduce the concentration of CH4 and CO in the synthesis gas. Since the methane and CO are a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of pure ATR (optionally in combination with pre-reformer) or POX, the invention employs a S/C ratio not higher than 2 in the reforming section. Preferably further steam is added downstream of the reforming and upstream of the shift, until an overall S/C ratio greater than 2, and preferably greater than 2.4, is reached so as to promote the progression of the shift reaction and the associated conversion of the carbon monoxide.

The use of the trim fuel solves the problem of rapidly controlling the furnace, but at the cost of increasing the CO2 emissions into the atmosphere. For some configurations of the invention, for example those comprising a steam reformer, the trim fuel represents the greatest contribution to the CO2 emissions in the atmosphere. This will be illustrated in the examples.

In a preferred embodiment of the invention, the trim fuel is not used and the fuel of the furnace is only the synthesis gas. The fuel fraction is consequently greater than in the case where the trim fuel is used, because it is required to provide also the combustion heat of the trim fuel with the fuel fraction.

In a first embodiment, the fuel fraction has a combustion heat substantially corresponding to the heat required by the furnace. In order to rapidly control the furnace, for example in order to quickly raise or lower the load when needed, the flowrate of the fuel fraction is suitably raised or lowered. This control, however, has the undesirable effect of varying the flowrate of the make-up gas, and therefore the production. In order to re-establish the initial production, it is necessary to increase or reduce the total flowrate of natural gas fed to the reforming section, which in turn requires control of the furnace. It may be understood how this procedure is operationally undesirable.

According to one aspect of the invention: the fuel fraction is produced in an overabundant amount with respect to the requirement of said at least one furnace, i.e. a surplus of synthesis gas to be used as fuel is produced with respect to the corresponding quantity of heat required by the furnace, and the surplus of fuel synthesis gas is exported from the process, i.e. is not used either as fuel fraction or as process fraction. The availability of synthesis gas in excess (for use as fuel) allows to rapidly regulate said at least one furnace without using, or using to a lesser degree, the trim fuel, with a further advantage in terms of reduction of the CO2 emissions.

For example, the surplus may be:

- exported as a further product (for example as hydrogen or as CO2-depleted fuel for consumption outside the ammonia plant) or
- conveyed to a storage buffer, or
- flared.

In order to rapidly control the furnace, for example in order to quickly raise or lower the load in the case of need, the flowrate of the synthesis gas surplus is suitably lowered or raised , without affecting either the fuel fraction or the process fraction.

The surplus of fuel synthesis gas may be taken from the fuel fraction, and therefore have the same composition and pressure as the fuel synthesis gas.

Alternatively, if a purification unit (for example a PSA unit) or a methanation unit is present, the surplus of fuel synthesis gas may be collected downstream of purification or methanation, so as to obtain greater purity of the surplus exported.

The surplus fuel may be separated from the tail gas of purification (PSA, or dryer + LNW), even though said solution is less preferred for two reasons:

the tail gas has a low pressure, therefore a compression is required to export said tail gas (with considerable energy expenditure and plant cost);

the tail gas contains CO, CO2 and CH4 in a concentration much greater than both the fuel synthesis gas and the purification product, therefore it has a less desirable composition.

The quantity of the surplus fuel synthesis gas is preferably >2%, more preferably >4%, and even more preferably >6% of the fuel fraction. If the surplus of the fuel synthesis gas is not exported, its quantity is preferably not greater than 15% of the fuel fraction, and even more preferably not greater than 10% of the fuel fraction, in order to prevent an excessive consumption thereof.

The invention obtains CO2 emissions which are less than 0.5 t/t (tonnes of CO2 emitted per tonne of ammonia produced); in preferred embodiments of the invention the emissions are less than 0.3 t/t or less than 0.2 t/t.

As will be illustrated in the examples, in some preferred embodiments the CO2 emissions may reach values less than 0.1 t/t or even 0.05 t/t, corresponding to a CO2 capture value close to 99%.

As regards the plant, the furnaces are advantageously equipped with dual-fuel burners able to burn both natural gas and synthesis gas. The invention may require the installation of an air separation unit (ASU) for the production of the enriched air and optionally nitrogen.

The invention may also be applied to ammonia/urea processes and plants. An ammonia/urea plant is a plant comprising a first ammonia synthesis section and a second section for synthesis of urea from ammonia and CO2, wherein at least a part of the ammonia produced in the first section feeds the second section. In this case also the CO2 separated during the decarbonation step feeds advantageously said second urea synthesis section.

The main advantages of the invention are listed below.

The separation of the CO2 is performed from a synthesis gas which has a high concentration of CO2 (15-25% mol) and is at a relatively high pressure, and therefore the separation of CO2 from this flow is much easier and requires a lower energy consumption than CO2 separated from combustion fumes.

The system according to the invention does not require solvent in order to capture CO2 from fumes.

The use of oxygen-enriched air gives rise to various advantages:

- it increases the heat value of the synthesis gas;
- combustion of the synthesis gas generates less fumes than the combustion of natural gas, for the same amount of heat released, because the combustion of hydrogen (contained in the synthesis gas) occurs with a reduction of the number of mols, unlike the combustion of methane, so that the convective current of the reformer is smaller and requires an induced draft (ID) fan which is less powerful;
- it limits the flue loss of nitrogen (which is a reagent), avoiding wastage of energy for N2 separation and compression; the generation of nitrogen for synthesis must not be increased;
- it allows a high temperature for conversion of the natural gas to be maintained, free from the constraint of avoiding the introduction of excessive nitrogen in relation to the stoichiometry of the NH3 synthesis (typical of conventional air-fired processes) with a high conversion of the methane resulting in minimal CO2 emissions.

In conventional plants with a secondary air-fed reformer, the process air is fed to said secondary reformer in stoichiometric quantities, i.e. in the quantity required to reach a H/N ratio of about 3 in the make-up gas. This means that

the air flowrate (in particular the quantity of oxygen introduced into the reformer) cannot be freely chosen, for example in order to achieve full conversion of the NG.

Instead, if the oxidant and the nitrogen are separately fed to the process, it is possible to choose the flowrate of oxidant so as to obtain complete conversion of the natural gas and optionally add, downstream, the nitrogen which is needed for the desired make-up gas composition. The advantage of full conversion is to produce a synthesis gas with a smaller methane content and therefore lower CO2 emissions.

Another advantage of the invention is that the greater flowrate of gas in the front end allows more heat to be recovered and more steam to be generated. The greater quantity of steam produced in the front end limits the duty of the respective auxiliary steam-generating apparatus; an advantage is that the fuel consumption (and potential source of CO2 emissions) is represented only by the primary reformer or fired heater. If the fuel of the reformer is replaced with synthesis gas (and if necessary the associated burners replaced) a substantial elimination or zeroing of the CO2 emissions is obtained.

Another advantage is that the invention does not require necessarily separation of hydrogen from the CO2-depleted syngas, i.e. purification of the CO2-depleted syngas into a gas which is rich in H2 and a waste gas, in order to obtain low CO2 emissions into the atmosphere. The CO2-depleted syngas may be used directly for ammonia synthesis after possible methanation.

In some embodiments it may be advantageous to perform a syngas gas purification in order to reduce the overall energy consumption of the process.

When applied to revamping of plants, the invention achieves significant synergies which allows the CO2 emissions to be reduced without production losses, limiting modifications and costs. This is because the invention:

- reduces greatly the gas flowrate in the front end, and therefore the

associated apparatus and (secondary, shift reaction, decarbonation or methanation) piping are suitable for a greater capacity;

- said greater capacity corresponds to the synthesis gas to be used as fuel;
- a high output temperature from the secondary reformer may be used (obtaining complete conversion of the methane), because the nitrogen is added separately from the oxygen; therefore the method according to the invention produces extra gas to be used as fuel without requiring costly modifications of the primary reformer, even when said reformer is substantially at the limit of its capacity;
- the CO2 removal section is de-bottlenecked because the invention increases the partial CO2 pressure and reduces the gas flowrate in the absorber;
- the combustion of the CO2-depleted syngas generates fewer fumes than the NG so that the convective current of the reformer and ID fan are less charged;
- it is necessary to modify only the front end, while the backend (synthesis gas compressor, ammonia synthesis, refrigerating section) is substantially unchanged.
- the process does not require intense purification of the synthesis gas in order to remove the inert components, it being sufficient to use the methanator (often the existing one); in particular, it is not necessary to perform any separation of the synthesis gas into an H2 and waste gas flow.

Description of the figures

Fig. 1 shows a first embodiment of the invention.

Fig. 2 shows a second embodiment.

Fig.3 shows a third embodiment.

Fig. 4 shows a fourth embodiment.

Description of preferred embodiments of the invention

Fig. 1 shows a process according to a mode of implementing the invention based on an oxygen autothermal reformer ATR and pre-reformer.

The blocks in Fig. 1 denote the following systems or apparatus:

AUX	charge pre-heater furnace and auxiliary boiler
PRE	pre-reformer
ATR	autothermal reformer
POX	partial oxidation reactor
SHF	shift section
CDR	CO2 removal section (decarbonation)
MET	methanator
SYN	synthesis section
HRU	hydrogen recovery section
ASU	air separation (fractioning) section

A charge 10 comprising natural gas and steam is preheated in AUX and converted into a synthesis gas 11 via the reformers PRE and ATR. The autothermal reformer ATR operates with a flow 22 of enriched air or oxygen.

The synthesis gas, which contains H2, CO and CO2, undergoes a shift reaction in SHF and then removal of CO2 in CDR. The section SHF may comprise shift treatments at different temperatures. The section CDR operates

for example with chemical/physical washing of the gas using an aqueous amine solution.

The section CDR produces a CO2-depleted syngas 12 and a flow 13 of CO2 which may be sequestered or used for other process purposes, for example in order to produce urea.

Preferably the synthesis gas 12 has the following composition: 98% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

A part 14 of said CO2-depleted syngas 12 is used as fuel in a furnace in the front end, for example in a charge heater (AUX block). The remaining part 18 of synthesis gas is further treated in the methanator MET.

In the example, the fuel fraction 14 of synthesis gas, together with a tail gas 15 of the HRU section, feeds one or more users of the block AUX via the fuel line 16. Optionally a suitable quantity of natural gas 17 (trim gas) is added to the gas 16.

Nitrogen 18 from the air separation section ASU is added to the process fraction 18 of the synthesis gas, after it has passed inside the methanator (optional).

The gas thus obtained, together with a flow of hydrogen 20 recovered from the HRU section, feeds the synthesis section SYN. Said synthesis section produces ammonia 23 and a flow 21 of purging gas treated in the section HRU for recovery of the hydrogen contained inside it.

The separation section ASU produces, in addition to the nitrogen 19, also the flow 22 of enriched air or oxygen for the autothermal reformer ATR.

Fig. 2 shows a process according to a preferred mode of implementing the invention based on primary reforming and ATR.

The block SMR in Fig, 1 denotes the primary reformer (or steam reformer) plus

auxiliary apparatus, for example steam generators. The remaining symbols in Fig. 2 correspond to the symbols in Fig. 1 and therefore the description is not repeated.

Fig. 2 also shows an optional line 15a for recycling part of the tail gas 15 from the unit HRU for feeding the primary reformer SMR.

Fig. 3 shows an ATR-based process, similar to Fig. 1, but comprising a purification of the process fraction of the synthesis gas in a section PUR, which in this example comprises a PSA unit.

The fuel fraction 14 separated from the CO2-depleted synthesis gas 12 is divided into a first portion 14a used as fuel in a furnace in the front end, for example in the block AUX, and a second portion 14b exported as excess fuel. The remaining part 18 of synthesis gas is further treated in the PSA unit.

A portion 23 of the effluent of the PSA unit is (optionally) exported as excess fuel. Said portion 23 has a greater hydrogen purity than the gas portion 14b.

In the example shown in Fig, 3, the portion 14a of synthesis gas separated as fuel fraction, together with a tail gas 25 of the PSA unit, feeds one or more users of the block AUX via the fuel line 26.

Fig. 4 shows a process based on POX, comprising purification of the process fraction of the synthesis gas in a section PUR comprising dryer and LNW (liquid nitrogen wash).

In a similar manner to the embodiment shown in Fig. 3, also in this case the fuel fraction 14 separated from the CO2-depleted synthesis gas 12 is split into a first portion 14a used as fuel for example in the block AUX, and a second portion 14b exported as excess fuel. Said portion 14a, together with a tail gas 35 of the section PUR, feeds one or more users of the block AUX via the fuel line 36. Said tail gas 35 results from the combination of the tail gas of the LNW and of the dryer.

The process according to the invention allows to produce ammonia with emissions of CO2 of about 0.1 t/t compared to about 0.7 t/t in the prior art.

All the configurations illustrated may be the result of revamping of an ammonia plant with air-fed secondary reformer.

In one embodiment, the revamping procedure comprises essentially the following steps:

installing the ASU unit in order to generate the flow 22 of oxygen or enriched air;

modifying the secondary reformer in order to accept said flow 22 instead of air;

increasing the fraction of natural gas intended for the process and reducing the fraction of natural gas intended for fuel;

revamping the existing section for desulphurization of the natural gas so as to increase the capacity thereof owing to the greater process gas flowrate;

revamping the existing section CDR so as to increase the capacity thereof owing to the greater quantity of CO2 to be separated.

It can be understood that the revamping does not require costly modifications to the reformer, the exchangers and piping of the front end and the shift section. This is due to the fact that the volumetric flowrate of the gas through the front end does not increase, despite the generation of the additional gas fraction (fuel fraction).

Example:

The following Table 1 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced.

Table 1 compares the following options:

(1) Plant of the prior art with primary reformer and air-fed secondary reformer.

(2) Plant of the prior art, as per option (1), with capturing of the CO2 from the fumes of the primary reformer.

(3) Plant according to the invention, as per Fig. 1.

(4) Plant according to the invention, as per Fig. 2.

Table 1

Option		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
NH3 production	MTD	3000	3000	3000	3000
Net Natural Gas consumption based on gas LHV (FEED+FUEL-Steam exported e.g. to urea)	Gcal/t NH3	6.7	7.4	7.0	6.9
	Gcal/t NH3		+0.7	+0.3	+0.2
CO2 captured in process	MTD	3600	3600	5200	5100
CO2 to atmosphere (contained in flue gas)	MTD	2100	200	200	200
CO2 to atmosphere (contained in flue gas)	t/t NH3	0.7	0.1	0.1	0.1
Main Equipment size					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	100	145	140
ASU O2 capacity	%	n/a	n/a	100	60
Flowrate of front end (secondary output/ ATR)	%	100	100	120	97

The table shows that the process according to the invention (option 3) requires a front end suitable for producing also the gas fraction to be used as fuel in the furnaces; in fact the quantity of CO2 captured in the process amounts to 5200 MTD compared to 3600 for options (1) and (2), and the synthesis gas flowrate in the front end is about 20% more than Fig. 1 and 2. Despite this, the consumption of the plant is much less than that of option (2) (7.0 instead of 7.4 Gcal/MT) and is competitive with the plant without capturing according to

option (1). The total duty of the furnaces is only 75% of option (1).

In option (4) the energy consumption obtained is less than in option (3), i.e. equal to 6.9 Gcal/MT, and also the cost of the plant is less. This because, in option (4), the quantity of CO2 separated in the process is less than in option (3); the duty of the furnaces is greater than in (3), but is comparable with that of options (1) and (2); the oxygen consumption is markedly less than (3); the flowrate in the front end is markedly less than (3) and comparable with (1) and (2).

The examples show how the novel process is more efficient and competitive than the prior art.

The example also shows the advantage of modifying a plant operating as per option (1), preferably implementing option (4). In fact, in this case the duty of the furnaces and the flowrate of the gases remain substantially unvaried, while the CO2 emissions are reduced. The invention thus achieves the object of minimizing the CO2 emissions of a conventional plant without losing ammonia production.

The following Table 2 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced, which is self-sufficient from the point of view of the steam and electric power. The process comprises the consumption relating to the compression of the CO2 sequestered up to the pressure of 100 bar. For each process, the natural gas consumption and the CO2 emissions indicated also consider the superheated steam production in AUX for driving all the turbines, and the production of the electric power necessary for the process.

Table 2 compares the following options:

(1) Plant according to the invention, with SMR+ATR as per Fig. 2, in the following variants:

a. with the overall S/C ratio = 2.7, shift composed of HTS and LTS,

methanator, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 1a, but without trim fuel.

(2) Plant according to the invention, with pre-reformer + ATR as per Fig. 3, in the following variants:

a. with the overall S/C ratio = 2, shift composed of MTS and LTS, PSA, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 2a, without trim fuel, with the Selectoxo process downstream of SHF and upstream of CDR for converting the residual CO.

(3) Plant according to the invention, with POX, as per Fig. 4, in the variants:

a. with the overall S/C ratio = 2, shift composed of MTS and LTS, LNW dryer, trim fuel with flowrate corresponding to 10% of required duty of the furnace;

b. as for 2a, without trim fuel, with selective catalytic oxidation of CO (Selectoxo™ process) downstream of the shift reaction and upstream of the CO2 removal.

Table 2

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
Daily production of NH3, MTD	3000	3000	3000	3000	3000	3000
Daily throughput of sequestered CO2, MTD	5600	5800	5100	5300	5350	5600
Net consumption of natural gas (for Example 1a), dimensionless	100%	100%	93%	93%	95%	95%

CO2 emissions into atmosphere per unit of ammonia produced, t CO2/t NH3	0.15	0.075	0.17	0.10	0.15	0.05
Distribution of the CO2 emissions						
- trim fuel	50%	zero	20%	zero	20%	zero
- CH4 slip in the process gas	15%	29%	40%	79%	30%	63%
- CO slip in the process gas	34%	69%	39%	19%	49%	34%
- CO2 slip in the process gas	1%	2%	1%	2%	1%	3%

In Table 2:

"Trim fuel" as defined in the patent;

"CH4 slip in the process gas" is the residual methane content of the synthesis gas produced in the front end (i.e. in SMR + ATR in option 1, in the pre-reformer + ATR in option 2, POX in option 3), quantified upstream of optional methanation.

"CO slip in the process gas" is the residual carbon monoxide content of the synthesis gas downstream of the shift section;

"CO2 slip in the process gas" is the residual carbon dioxide content of the synthesis gas downstream of the CO2 removal section;

Several comments may be made in view of Table 2:

- In the case of SMR+ATR in option 1a, the trim fuel provides the greatest percentage of the CO2 emissions; avoiding the trim fuel by exporting surplus fuel enables the emissions to be significantly reduced to less than 0.1

t/t, as shown in the Table for option 1b; at the same time, the quantity of sequestered CO2 increases from 5600 to 5800 MTD.

- In the case of SMR+ATR, the CO slip in the process gas provides the second greatest percentage of the CO2 emissions in option 1a, and provides the greatest percentage in option 1b; application of the Selectoxo process to option 1a or 1b would significantly reduce the CO2 emissions; the CH4 slip in the process gas and the CO2 slip in the process gas provides a smaller percentage of the CO2 emissions.

- The overall energy consumption of the options based on ATR and POX + purification (2 and 3) is decidedly lower than that of the options based on SMR + ATR (1a and 1b); this is mainly due to the synthesis gas purification (which improves the efficiency of the synthesis section and avoids the purge); the quantity of CO2 sequestered in these options (2a, 3a; or 2b, 3b) is consequently less than in options 1a or 1b.

- The emissions due to the use of the trim fuel in options 2a (ATR) and 3a are of about 20% of the total emissions, much less than in option 1a, by way of confirmation of the fact that the heat required by the furnace in these two options is much less than in option 1a.

- In the embodiments with ATR or POX, the residual CO and CH4 are of higher relevance owing to the lower S/C ratio at which ATR and POX operate compared to SMR+ATR; POX operates at a higher temperature than ATR, which results in a smaller residual amount of CH4, but in a greater residual amount of CO.

- In both the options 2b and 3b, the improvement achieved by selective oxidation of CO, in order to reduce the CO slip, and by avoiding trim fuel, is evident.

- It should be noted that both POX and ATR achieve very low emissions - as low as 0.05 for POX and 0.1 for ATR - comparable with those achieved by

SMR+ATR, but with lower energy consumption, and therefore preferable.

The above example shows how the invention is able to achieve extremely low CO2 emission levels, corresponding to almost total capture (>98%), while maintaining competitive energy consumption levels.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/052358

A. CLASSIFICATION OF SUBJECT MATTER
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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)
C01B C01C

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, CHEM ABS Data, 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 A	US 2004/234426 A1 (REDDY SATISH [US] ET AL) 25 November 2004 (2004-11-25) paragraphs [0023] - [0027], [0031], [0032], [0034]; figures 2,3	1,3,5-8, 10,14-18 2,4,9, 11-13
Y A	WO 2010/018550 A1 (AIR LIQUIDE [FR]; VAKIL TARUN D [US]; WOLF ULRICH [DE]) 18 February 2010 (2010-02-18) page 3, line 23 - page 4, line 19; claim 7; figures 2,3 page 11, line 20 - page 12, line 8 page 17, lines 15-27	1,3-7, 11,12, 15-18 2,8-10, 13,14
Y A	US 2015/031916 A1 (KISS GUENTER HANS [CH]) 29 January 2015 (2015-01-29) paragraphs [0012] - [0020]; figure 1	1,3-7, 11,12, 14-18 2,8-10, 13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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Page 230 of 356

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/052358

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(54) Title: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

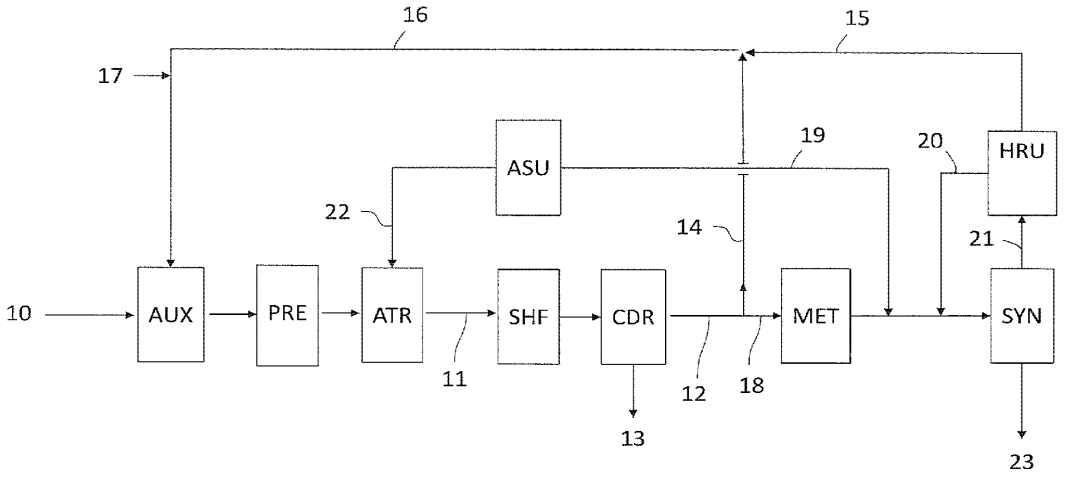


FIG. 1

(57) Abstract: Process for the synthesis of ammonia from natural gas comprising conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or oxygen, into a synthesis gas (11), and treatment of the synthesis gas (11) with shift reaction and decarbonation, wherein a part of the CO2-depleted synthesis gas, obtained after decarbonation, is separated and used as fuel fraction for one or more furnaces of the conversion section, and the remaining part of the gas is used to produce ammonia.

[Continued on next page]

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Process for the synthesis of ammonia with low emissions of CO2 in atmosphere

Field of application

The invention relates to the field of ammonia synthesis plants fed with natural gas (NG).

Prior art

The ammonia synthesis plants of the type considered here comprise a section adapted to convert the natural gas into a make-up gas containing hydrogen and nitrogen, and a synthesis section wherein said make-up gas reacts catalytically at high pressure to produce ammonia.

The section which generates said make-up gas is referred to in the technical language as the "front end". The term "back end" is instead used to denote the section for ammonia synthesis and the respective cooling section intended to cool the effluent of the synthesis section in order to separate the ammonia.

In the front end, the desulphurized natural gas undergoes reforming, resulting in a gas containing essentially hydrogen, carbon monoxide CO and carbon dioxide CO2. Said gas then undergoes a shift reaction which converts CO into CO2; removal of CO2 (decarbonation) and preferably methanation.

The reforming process, in a common type of plant, comprises primary steam reforming and a subsequent catalytic air-fired secondary reforming. The primary reformer is heated by burners fuelled by a part of the available natural gas. In the secondary reformer the effluent from the primary reformer burns due to contact with the oxygen contained in the air. In some plants other reforming configurations are used, for example an autothermal reformer (ATR) preceded by a furnace for heating the charge, i.e. the gaseous mixture fed to

said reformer.

The above described ammonia plants result in significant emissions of CO2 into the atmosphere, overall in the region of 100 million tonnes of CO2 per year. One of the main sources of CO2 emission consists in the combustion fumes of the primary reformer and other burner furnaces if any, for example auxiliary heaters.

For environmental reasons, it is required to minimize the CO2 emissions from the fumes of the NH3 plants. The problem affects in particular the older ammonia plants which are less efficient than the new ones and have greater CO2 flue emissions in relation to the quantity of ammonia produced. It is also necessary that the reduction of the emissions should not increase excessively the costs for production of the ammonia.

According to the present state of the art, the processes for capturing CO2 from fumes are based on washing with solvents (for example the solvent KS-1™ produced by Mitsubishi). The associated plants are, however, costly and complicated, have a high energy consumption and require expensive solvent. Therefore these CO2 capturing processes cannot be applied to the plants considered here since they would increase excessively the costs for production of the ammonia.

In some ammonia synthesis processes of the prior art, part of the fuel may be supplied by a purge flow obtained, for example, from a cryogenic purification section of the synthesis gases or from a PSA unit. Said purge flow may have a reduced CO2 content. However, said purge flow accounts for a small amount of the total fuel and does not solve the problem of the CO2 emissions in the atmosphere.

Summary of the invention

The object of the invention is to provide a method for conducting ammonia synthesis processes with CO2 emissions into the atmosphere which are

greatly reduced compared to the prior art. Another object of the invention is to provide a method for revamping the existing plants, of the type using air-fed secondary reformers able to reduce drastically the CO2 emissions into the atmosphere.

The objects are achieved with a process and a revamping method according to the claims.

According to the invention, a process for synthesis of ammonia from natural gas comprises:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, to form a synthesis gas containing hydrogen, CO and CO2;

a treatment of said synthesis gas comprising at least one shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas, obtaining a make-up gas containing nitrogen and hydrogen in a suitable molar ratio for ammonia synthesis,

characterized by:

separation of a part of said CO2-depleted synthesis gas, obtaining a fuel fraction of the synthesis gas, wherein said fuel fraction is fed as fuel to at least one furnace.

The invention also relates to a method for revamping a plant originally comprising a reforming section which includes a primary steam reformer and air-fired secondary reformer, and treatment of the synthesis gas comprising a shift reaction of carbon monoxide into carbon dioxide, decarbonation and

optionally methanation. The revamping method comprises at least:

providing a flow of enriched air or oxygen and using said flow as an oxidant for the secondary reformer instead of the air;

separating a part of the synthesis gas downstream of decarbonation,

feeding said part of the synthesis gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

The term "furnace" is understood as meaning an apparatus chosen from among: a steam reformer or a charge preheater or a steam generator or a steam superheater. These apparatus, which operate by means of combustion, are identified by the term "fired heater". Said furnace in some embodiments forms part of the section for converting the natural gas into synthesis gas. In combined ammonia/urea plants said furnace may form part of the urea section.

The portion of synthesis gas which is separated and sent to said at least one furnace is termed fuel fraction of the gas available after the shift step. Preferably, said fuel fraction is comprised between 1% and 40% of the available gas, more preferably between 10% and 30% and even more preferably between 20% and 30%. For example in a preferred embodiment the fuel fraction is equal to 30%. The remaining part, which is intended to be converted into ammonia, is called process fraction.

It should be noted that said fuel fraction is relatively high, for example about 1/3 of the total. The invention in fact envisages that a non-negligible portion of synthesis gas is allocated to fuel in order to reduce the CO2 emissions. This results in the need to produce an additional quantity of synthesis gas, but, as will be explained more clearly below with the aid of the examples, this necessity is compensated for by the advantages of the invention.

The separation of the fuel fraction is advantageously performed by splitting a

process flow, for example a process gas after shift and decarbonation. As a result of said splitting, the fuel fraction and the remaining part of the gas, also called process fraction, have the same composition.

It should be noted that the present invention envisages deliberately allocating a part of the process flow to the fuel fraction, the fuel fraction being directly separated from the process flow and having the same composition. The prior art, on the other hand, teaches only allocating as fuel any purge streams derived from purification processes and containing methane. The said synthesis gas with a low CO2 content (CO2-depleted syngas) preferably contains no more than 1000 ppm by volume (0.1%) of CO2. Said gas is composed essentially of hydrogen ((H2) with any small residual quantities of CO and CH4, typically less than 2% by volume and preferably less than 1%.

The combustion of said gas is substantially free from production of CO2. In fact, the combustion of the hydrogen does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The invention suggests using a process gas part as fuel for one or more furnaces of the reforming section, differently from the prior art which, for this purpose, uses part of the natural gas, i.e. a hydrocarbon. The process gas part (fuel fraction) is suitably separated after a CO2 removal treatment and, as explained further above, it contains essentially hydrogen which may burn without forming CO2. Consequently it can be understood that the invention allows the CO2 emissions into the atmosphere to be drastically reduced.

Said oxygen-enriched air preferably contains at least 50% oxygen by volume and more preferably at least 90% oxygen by volume and even more preferably at least 95%. The advantages of a high oxygen content in the enriched air are as follows: greater calorific power of the synthesis gas; smaller flow of flue discharge gas; smaller volumetric flow through the apparatus of the conversion section and, consequently, smaller apparatus.

The CO2-depleted synthesis gas preferably forms all - or substantially all - the fuel of the furnaces used for the process. In some embodiments, however, it is preferred to keep a small amount of natural gas which is called "trim fuel" of the furnace. Preferably said small quantity accounts for not more than 15%, more preferably not more than 10%, of the total combustion heat (duty) of the furnace. The trim fuel allows the furnace to be rapidly controlled, for example in order to quickly raise or lower the load if needed.

Said percentage of the combustion heat may be expressed as the product between the flowrate (kg/s or mol/s) and the calorific power (J/kg or J/mol).

According to some embodiments of the invention, methanation of the synthesis gas is performed downstream of decarbonation. The methanation step converts residual CO and CO2 into CH4, consuming H2, in accordance with the reactions CO + 3H2 → CH4 + H2O e CO2 + 4H2 → CH4 + 2H2O.

Preferably, the separation of the fuel fraction from the CO2-depleted synthesis gas is performed before (upstream of) of said methanation step.

The advantage of separating the fuel fraction before methanation is that of not oversizing the methanation section of the fuel fraction, and of not losing the methanation heat of the fuel fraction. Moreover, for the same furnace heat requirement and the same gas temperature, the fuel fraction is slightly less if removed before methanation.

There are no disadvantages as regards CO2 emissions into atmosphere, which are the same by using as fuel both the gas upstream of the methanator and the gas downstream of the methanator, for the same flowrate. In case of nitrogen addition, the fuel fraction is separated before adding nitrogen. The advantage is a greater calorific power of the synthesis gas used as fuel, which does not contain nitrogen, or contains a smaller amount thereof.

After separating the fuel fraction, the CO2-depleted synthesis gas may be optionally treated in a purification section comprising, for example, a PSA unit

or comprising a dryer followed by a cryogenic unit.

The purification section produces at least one stream of ammonia synthesis gas with a reduced content of inerts, and at least one waste stream containing CO, and CH4. The waste stream may also contain H2 and N2. In some embodiments, at least part of the waste gas of said purification section is used as fuel together with the fuel fraction. Consequently, the fuel fraction may be reduced.

The advantage of the purification unit is that of reducing the inerts content in the make-up gas, resulting in known advantages for the ammonia synthesis, including smaller consumption for circulation and a reduction (or even elimination) of the purge flow of the ammonia synthesis loop.

According to the invention, the fuel fraction is advantageously separated upstream of the purification unit. Consequently, only the synthesis gas portion supplied to the ammonia synthesis undergoes treatment in the purification section which, without having to process the synthesis gas corresponding to the fuel fraction, may be realized with much smaller dimensions. The advantage of separating the fuel fraction upstream of the purification unit is that of avoiding oversizing of the purification unit and the corresponding consumption for the fuel fraction of the synthesis gas. Another advantage is the possibility of controlling separately the fuel fraction and the purification unit.

There is no disadvantage in separating the fuel fraction upstream of the purification from the point of view of the CO2 emissions into atmosphere, since the CO, CO2 and CH4 contained in the synthesis gas of the fuel fraction would be separated by the purification unit to form the waste stream and used as fuel.

Advantageously, the purification unit does not need to have an excessively high hydrogen recovery, because the hydrogen "lost" in the waste gas is used

as fuel and does not produce CO2 emissions into atmosphere. The fuel fraction of the synthesis gas is consequently regulated.

Preferably, however, the purification unit has a sufficiently high hydrogen recovery such that the fuel fraction accounts for at least 30%, preferably at least 40%, even more preferably at least 50% of the furnace duty. The applicant has found that this condition is advantageous for the control of the furnace itself independently of the control of the purification unit.

The purification section may comprise selective adsorption of the undesirable components onto a solid. In some embodiments said purification section comprises a PSA (pressure swing adsorption) unit which uses molecular sieves for separating CO, CH4, Ar, H2O and residual CO2. In other embodiments said section comprises at least one dryer for separating residual CO2 and water, followed by a cryogenic unit for separation of CO, CH4 and Ar. The cryogenic separation unit is preferably a Liquid Nitrogen Wash (LNW) unit.

A PSA unit typically produces a single flow of purified product, substantially at the feed pressure, and a single stream of waste gas, at a pressure much lower than the feed pressure. Said waste stream contains CO, CH4, Ar, H2O and residual CO2, and may contain H2 and N2.

If the purification section comprises dryer and LNW, the purified product may emerge as one or more streams, and may already contain H2 and N2 in a suitable ratio for the synthesis of ammonia.

The dryer has a tail gas, product of regeneration of the molecular sieves used for capturing mainly H2O and the traces of residual CO2 contained in the feed, which would freeze during the cryogenic treatment in the LNW unit. The dryer may be regenerated with a nitrogen flow (from the air separation unit). In this case the tail gas containing N2, H2O and CO2 may be discharged into atmosphere or combined with the tail gas of the LNW described below.

The LNW also has at least one tail gas which contains the bottom end product of the LNW absorption column, containing CH4 and CO, in addition to N2 and H2. The discharge gas of the LNW may be conveyed away as fuel.

The tail gas of the LNW may be used at least partly for the regeneration of the dryer before being conveyed away as fuel.

The synthesis gas with a low content of inerts may be conveyed away for ammonia synthesis.

Methanation is an exothermic reaction, but there is not a substantially large amount of reaction heat and it is usually not recovered.

Methanation therefore leaves a small quantity of methane in the synthesis gas (methane slip). The presence of said small quantities of methane in the synthesis gas is not a problem for the purposes of ammonia production, since methane is inert to the synthesis reaction. Methane accumulates in the purge flow of the synthesis loop. However, by using the purge flow of the synthesis loop as fuel, the methane contained therein constitutes a source of CO2, albeit of small entity.

The carbon monoxide contained in the synthesis gas also constitutes a source of CO2, albeit of small entity, both owing to combustion of the synthesis gas used as fuel, and owing to combustion of the waste gas of a purification unit, where present.

In some embodiments of the invention, in order to reduce also this source of CO2 (i.e. the emissions caused by the presence of residual carbon monoxide of the synthesis gas), the process comprises a catalytic purification which selectively converts the CO into CO2 upstream of decarbonation. Selective conversion of the carbon monoxide may be obtained, for example, using the process known as Selectoxo™ which operates with the reaction CO + 1/2 O2 → CO2. The oxygen for selective oxidation of the CO may be a part of the mentioned enriched-air or oxygen flow.

An advantage of said selective conversion of CO into CO2 is that at least part of the residual CO from the shift is converted into CO2 and removed during decarbonation. Consequently, the combustion of the synthesis gas, of the synthesis loop purge flow, or of the purification waste gas, produces a smaller quantity of CO2.

According to the invention, the CO2 flue emissions are mainly determined by the CO, CO2 and CH4 content of the synthesis gas downstream of decarbonation, as well as by the optional trim fuel flow which will be described below.

The combustion of said gas is substantially free from CO2 production. In fact, the hydrogen combustion does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The CO2 production is also derived from the combustion of the methane contained in the synthesis loop purge flow.

In case a purification unit is present, CO2 production is also derived from the combustion of CO, CH4 and residual CO2 of the discharge gas.

According to one aspect of the invention, the fuel fraction is produced in excess compared to the fuel required for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and the regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported by the process.

The conversion of the natural gas into synthesis gas may be performed using different techniques.

According to some embodiments of the invention, the step of natural gas conversion into synthesis gas comprises primary reforming followed by secondary reforming. In some embodiments, more preferably, the conversion

step comprises a catalytic autothermal reforming (ATR), optionally preceded by a preliminary reforming (pre-reforming). An ATR without preliminary reforming is also called "pure ATR". Advantageously, in these embodiments, at least a part of the synthesis gas fuel fraction feeds a furnace for pre-heating the gas prior to autothermal reforming.

The advantage of using ATR, pure or in combination with a pre-reformer, consists in the smaller heat requirement of the furnace compared to the combination of the ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the ATR feed and of the optional pre-reformer according to the invention is suitably chosen at a value not greater than 650°C, lower than the output temperature of the primary reformer, and due to the fact that, in the preheating furnace, there is no progression of the steam reforming reaction (which is endothermic).

A pure ATR, or ATR in combination with a pre-reformer, may advantageously operate with a steam/carbon (S/C) ratio less than that of a primary reformer. Preferably, said S/C ratio is not greater than 2, more preferably not greater than 1.5, even more preferably not greater than 1. This also helps reduce the heat required by the furnace for preheating the feed of the ATR and optional pre-reformer.

In the case of ATR without primary reformer, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

In some embodiments the step for converting the natural gas into synthesis gas comprises a non-catalytic POX (partial oxidation) step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds a furnace for preheating the gas before said partial non-catalytic oxidation or for steam generation or steam superheating.

The advantage of using a POX consists in the smaller heat requirement of the furnace compared to the combination of an ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the POX feed according to the invention is suitably chosen at a value not higher than 500°C, markedly lower than the output temperature of the primary reformer, and due to the fact that in the preheating furnace there is no progression of the steam reforming reaction (which is endothermic). Moreover, POX may advantageously use a S/C ratio lower than that of a primary reformer, preferably not greater than 2, more preferably not greater than 1, even more preferably not greater than 0.5. This also helps reduce the heat required by the preheating furnace.

In the case of POX, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

The reduction in the heat required by the preheating furnace for a POX and for a pure ATR compared to an ATR in combination with a primary reformer provides the following advantages: the fuel fraction of the synthesis gas is less, and it is possible to reduce the quantity of trim fuel, therefore lower CO2 flue emissions may be obtained.

Both in the case of POX with optional purification unit of the synthesis gas and in the case of ATR without primary reformer and with optional purification unit of the synthesis gas, it is preferable to select a purification unit with high hydrogen recovery, for example a liquid nitrogen wash, so as to ensure that the fuel fraction of the synthesis gas is sufficiently large to control the furnace independently of control of the purification unit.

Another advantage of the POX and ATR without primary reformer, consequence of both the smaller fuel fraction and the smaller steam/carbon ratio, is the smaller autogenous steam production, which reduces the heat

required for the associated overheating, the fuel fraction, the CO2 flue emissions and the total natural gas consumption.

The smaller autogenous steam production may result in a lack of steam for driving the turbines or of electricity for powering the motors of the machines. The missing energy may be conveniently imported from outside the plant as electricity with reduced CO2 emissions, for example generated by renewable sources. It should be pointed out that this synergy is not possible if the process already produces an excess of steam or energy, for example in the case of combination of primary reformer and ATR with a fairly large fuel fraction.

In some embodiments the step of converting the natural gas into synthesis gas also comprises a steam reforming step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds the burners of the reformer.

A part of the fuel fraction may be allocated, in some embodiments, to furnaces for the production and/or superheating of steam.

The invention also allows to produce the electricity necessary for the synthesis of ammonia or of its derivatives (for example urea) with low emissions of CO2, using as fuel CO2-depleted synthesis gas, for example in the following ways:

- expansion in a turbo generator of a flow of steam produced in a steam generator or steam superheater, fed by the CO2-depleted synthesis gas as fuel;

- combustion in a gas turbine or in a gas engine, fed by the CO2-depleted synthesis gas as fuel.

Generally, in ammonia processes, a purging gas is extracted from the ammonia synthesis loop, in order to remove the inert substances from the synthesis loop, and said purging gas is treated with a process for recovery of

the hydrogen contained in it (HRU). Said recovery process generates a hydrogen-rich gas which may be reused for synthesis and a tail gas containing most of the methane initially contained in the purging gas. The methane in the tail gas is practically all that contained in the process fraction of the synthesis gas. Normally said tail gas, given its relatively high methane content, is used exclusively as fuel. This use of tail gas, however, generates CO2 emissions.

According to one aspect of the invention at least a part of said tail gas is recycled as process gas during the natural gas conversion step, for example during the reforming or partial oxidation step. An associated advantage is a further reduction in the CO2 emissions.

In some embodiments a part of the said CO2-depleted synthesis gas is treated in a nitrogen (N2) separation unit, preferably a membrane unit, obtaining a nitrogen-depleted synthesis gas and a nitrogen-rich flow; at least a part of the nitrogen-depleted synthesis gas (preferably all of it) is used as fuel; the remaining part is fed to the ammonia synthesis together with the nitrogen-rich flow.

This configuration is particularly advantageous if the O2-enriched air does not have a very high purity (for example less than 95% of O2) and/or if the natural gas contains nitrogen. Three benefits are obtained: an increase in the calorific power of the fuel gas, a reduction in the flow of combustion fumes (and the power of the respective ID fan) and conservation of the nitrogen which is a reagent for the ammonia. The membrane nitrogen separation unit is further preferred because said unit may operate using the pressure difference between the synthesis gas (produced at high pressure) and the combustion in the furnace (which occurs at atmospheric pressure). Moreover, the nitrogen-rich flow, which is used for synthesis, does not lose pressure.

The configuration described above, which envisages separation of the nitrogen from the synthesis gas, is applicable also in a conventional process, with primary steam reformer and secondary air-fired reformer, resulting in the

advantage that it is not required to modify or enlarge the air compressor. However, with a secondary air-fired reformer and without modifying the compressor, and therefore without being able to increase the air flow, the additional fraction of synthesis gas (required as fuel) would have to be produced by increasing the capacity of the primary reformer and/or installing a gas-heated reformer (GHR), both solutions being very costly. For these reasons, the nitrogen separation described is particularly preferred in combination with the use of the enriched air during conversion of the natural gas into synthesis gas.

In some embodiments, it is envisaged expanding, with production of mechanical work, the CO2-depleted synthesis gas after optionally heating it.

Said gas is available at a pressure higher than the pressure required for combustion in a furnace and therefore it may be expanded in a suitable machine, such as an expander or a turbine, producing mechanical work. For example, said expansion may be from about 25 bar to about 3 bar. The gas has a high specific volume given that it comprises essentially H2 and for this reason its expansion may generate a considerable amount of power. The power obtained may cover partly the process requirements, making it more efficient.

In some embodiments the shift step comprises two steps at different temperatures, for example preferably one high-temperature shift (HTS), for example carried out using an iron-based catalyst, followed by a low-temperature shift (LTS) or medium-temperature shift (MTS), for example carried out using a copper-based catalyst. The associated advantage is that of obtaining the maximum conversion of the CO into CO2, which will then be separated during the decarbonation step, so as to obtain the minimum residual CO content in the synthesis gas used as fuel. Since the CO is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In some embodiments, in which a relatively low overall S/C ratio is used, for example <2.7, the shift preferably comprises two steps in series carried out over catalyst suitable to operate with a low steam content, for example a copper-based catalyst. In this configuration, the first step consists of a medium temperature shift (MTS), which is preferably pseudo-isothermal and operates in the temperature range of 200-320°C, and the second step is a low temperature shift (LTS) operating in the temperature range 180-250°C.

The conversion of the natural gas into synthesis gas, for example by means of reforming, is preferably performed at a pressure lower than 50 bar, more preferably lower than 40 bar, and even more preferably lower than 30 bar.

Generally the prior art teaches the preference for high conversion pressures, in order to increase the capacity of the conversion section (front end) and reduce the consumption of synthesis gas compression. The present invention is instead preferably implemented with low conversion pressures in order to obtain the maximum conversion of the methane, since the steam reforming reaction is favoured at a lower pressure, so as to have the minimum residual methane content in the synthesis gas used as fuel. Since the methane is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of ATR, a high methane conversion is also obtained by operating at a relatively high output temperature, >950°C, preferably >1000°C, even more preferably > 1030°C.

In the case of POX, a high methane conversion is also obtained by operating at a relatively high output temperature, >1200°C, preferably >1300°C.

In some embodiments the overall steam/carbon (S/C) ratio during conversion is greater than 2.0, preferably greater than 2.2 and more preferably greater than 2.7. Generally the prior art teaches a preference for low S/C ratios in order to increase the capacity of the conversion section (front end). The

invention instead envisages a relatively high S/C ratio in order to maximize the conversion of the methane and the CO during the shift step and reduce the concentration of CH4 and CO in the synthesis gas. Since the methane and CO are a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of pure ATR (optionally in combination with pre-reformer) or POX, the invention employs a S/C ratio not higher than 2 in the reforming section. Preferably further steam is added downstream of the reforming and upstream of the shift, until an overall S/C ratio greater than 2, and preferably greater than 2.4, is reached so as to promote the progression of the shift reaction and the associated conversion of the carbon monoxide.

The use of the trim fuel solves the problem of rapidly controlling the furnace, but at the cost of increasing the CO2 emissions into the atmosphere. For some configurations of the invention, for example those comprising a steam reformer, the trim fuel represents the greatest contribution to the CO2 emissions in the atmosphere. This will be illustrated in the examples.

In a preferred embodiment of the invention, the trim fuel is not used and the fuel of the furnace is only the synthesis gas. The fuel fraction is consequently greater than in the case where the trim fuel is used, because it is required to provide also the combustion heat of the trim fuel with the fuel fraction.

In a first embodiment, the fuel fraction has a combustion heat substantially corresponding to the heat required by the furnace. In order to rapidly control the furnace, for example in order to quickly raise or lower the load when needed, the flowrate of the fuel fraction is suitably raised or lowered. This control, however, has the undesirable effect of varying the flowrate of the make-up gas, and therefore the production. In order to re-establish the initial production, it is necessary to increase or reduce the total flowrate of natural gas fed to the reforming section, which in turn requires control of the furnace. It may be understood how this procedure is operationally undesirable.

According to one aspect of the invention: the fuel fraction is produced in an overabundant amount with respect to the requirement of said at least one furnace, i.e. a surplus of synthesis gas to be used as fuel is produced with respect to the corresponding quantity of heat required by the furnace, and the surplus of fuel synthesis gas is exported from the process, i.e. is not used either as fuel fraction or as process fraction. The availability of synthesis gas in excess (for use as fuel) allows to rapidly regulate said at least one furnace without using, or using to a lesser degree, the trim fuel, with a further advantage in terms of reduction of the CO2 emissions.

For example, the surplus may be:

- exported as a further product (for example as hydrogen or as CO2-depleted fuel for consumption outside the ammonia plant) or
- conveyed to a storage buffer, or
- flared.

In order to rapidly control the furnace, for example in order to quickly raise or lower the load in the case of need, the flowrate of the synthesis gas surplus is suitably lowered or raised , without affecting either the fuel fraction or the process fraction.

The surplus of fuel synthesis gas may be taken from the fuel fraction, and therefore have the same composition and pressure as the fuel synthesis gas.

Alternatively, if a purification unit (for example a PSA unit) or a methanation unit is present, the surplus of fuel synthesis gas may be collected downstream of purification or methanation, so as to obtain greater purity of the surplus exported.

The surplus fuel may be separated from the tail gas of purification (PSA, or dryer + LNW), even though said solution is less preferred for two reasons:

the tail gas has a low pressure, therefore a compression is required to export said tail gas (with considerable energy expenditure and plant cost);

the tail gas contains CO, CO2 and CH4 in a concentration much greater than both the fuel synthesis gas and the purification product, therefore it has a less desirable composition.

The quantity of the surplus fuel synthesis gas is preferably >2%, more preferably >4%, and even more preferably >6% of the fuel fraction. If the surplus of the fuel synthesis gas is not exported, its quantity is preferably not greater than 15% of the fuel fraction, and even more preferably not greater than 10% of the fuel fraction, in order to prevent an excessive consumption thereof.

The invention obtains CO2 emissions which are less than 0.5 t/t (tonnes of CO2 emitted per tonne of ammonia produced); in preferred embodiments of the invention the emissions are less than 0.3 t/t or less than 0.2 t/t.

As will be illustrated in the examples, in some preferred embodiments the CO2 emissions may reach values less than 0.1 t/t or even 0.05 t/t, corresponding to a CO2 capture value close to 99%.

As regards the plant, the furnaces are advantageously equipped with dual-fuel burners able to burn both natural gas and synthesis gas. The invention may require the installation of an air separation unit (ASU) for the production of the enriched air and optionally nitrogen.

The invention may also be applied to ammonia/urea processes and plants. An ammonia/urea plant is a plant comprising a first ammonia synthesis section and a second section for synthesis of urea from ammonia and CO2, wherein at least a part of the ammonia produced in the first section feeds the second section. In this case also the CO2 separated during the decarbonation step feeds advantageously said second urea synthesis section.

The main advantages of the invention are listed below.

The separation of the CO2 is performed from a synthesis gas which has a high concentration of CO2 (15-25% mol) and is at a relatively high pressure, and therefore the separation of CO2 from this flow is much easier and requires a lower energy consumption than CO2 separated from combustion fumes.

The system according to the invention does not require solvent in order to capture CO2 from fumes.

The use of oxygen-enriched air gives rise to various advantages:

- it increases the heat value of the synthesis gas;
- combustion of the synthesis gas generates less fumes than the combustion of natural gas, for the same amount of heat released, because the combustion of hydrogen (contained in the synthesis gas) occurs with a reduction of the number of mols, unlike the combustion of methane, so that the convective current of the reformer is smaller and requires an induced draft (ID) fan which is less powerful;
- it limits the flue loss of nitrogen (which is a reagent), avoiding wastage of energy for N2 separation and compression; the generation of nitrogen for synthesis must not be increased;
- it allows a high temperature for conversion of the natural gas to be maintained, free from the constraint of avoiding the introduction of excessive nitrogen in relation to the stoichiometry of the NH3 synthesis (typical of conventional air-fired processes) with a high conversion of the methane resulting in minimal CO2 emissions.

In conventional plants with a secondary air-fed reformer, the process air is fed to said secondary reformer in stoichiometric quantities, i.e. in the quantity required to reach a H/N ratio of about 3 in the make-up gas. This means that

the air flowrate (in particular the quantity of oxygen introduced into the reformer) cannot be freely chosen, for example in order to achieve full conversion of the NG.

Instead, if the oxidant and the nitrogen are separately fed to the process, it is possible to choose the flowrate of oxidant so as to obtain complete conversion of the natural gas and optionally add, downstream, the nitrogen which is needed for the desired make-up gas composition. The advantage of full conversion is to produce a synthesis gas with a smaller methane content and therefore lower CO2 emissions.

Another advantage of the invention is that the greater flowrate of gas in the front end allows more heat to be recovered and more steam to be generated. The greater quantity of steam produced in the front end limits the duty of the respective auxiliary steam-generating apparatus; an advantage is that the fuel consumption (and potential source of CO2 emissions) is represented only by the primary reformer or fired heater. If the fuel of the reformer is replaced with synthesis gas (and if necessary the associated burners replaced) a substantial elimination or zeroing of the CO2 emissions is obtained.

Another advantage is that the invention does not require necessarily separation of hydrogen from the CO2-depleted syngas, i.e. purification of the CO2-depleted syngas into a gas which is rich in H2 and a waste gas, in order to obtain low CO2 emissions into the atmosphere. The CO2-depleted syngas may be used directly for ammonia synthesis after possible methanation.

In some embodiments it may be advantageous to perform a syngas gas purification in order to reduce the overall energy consumption of the process.

When applied to revamping of plants, the invention achieves significant synergies which allows the CO2 emissions to be reduced without production losses, limiting modifications and costs. This is because the invention:

- reduces greatly the gas flowrate in the front end, and therefore the

associated apparatus and (secondary, shift reaction, decarbonation or methanation) piping are suitable for a greater capacity;

- said greater capacity corresponds to the synthesis gas to be used as fuel;
- a high output temperature from the secondary reformer may be used (obtaining complete conversion of the methane), because the nitrogen is added separately from the oxygen; therefore the method according to the invention produces extra gas to be used as fuel without requiring costly modifications of the primary reformer, even when said reformer is substantially at the limit of its capacity;
- the CO2 removal section is de-bottlenecked because the invention increases the partial CO2 pressure and reduces the gas flowrate in the absorber;
- the combustion of the CO2-depleted syngas generates fewer fumes than the NG so that the convective current of the reformer and ID fan are less charged;
- it is necessary to modify only the front end, while the backend (synthesis gas compressor, ammonia synthesis, refrigerating section) is substantially unchanged.
- the process does not require intense purification of the synthesis gas in order to remove the inert components, it being sufficient to use the methanator (often the existing one); in particular, it is not necessary to perform any separation of the synthesis gas into an H2 and waste gas flow.

Description of the figures

Fig. 1 shows a first embodiment of the invention.

Fig. 2 shows a second embodiment.

Fig.3 shows a third embodiment.

Fig. 4 shows a fourth embodiment.

Description of preferred embodiments of the invention

Fig. 1 shows a process according to a mode of implementing the invention based on an oxygen autothermal reformer ATR and pre-reformer.

The blocks in Fig. 1 denote the following systems or apparatus:

AUX	charge pre-heater furnace and auxiliary boiler
PRE	pre-reformer
ATR	autothermal reformer
POX	partial oxidation reactor
SHF	shift section
CDR	CO2 removal section (decarbonation)
MET	methanator
SYN	synthesis section
HRU	hydrogen recovery section
ASU	air separation (fractioning) section

A charge 10 comprising natural gas and steam is preheated in AUX and converted into a synthesis gas 11 via the reformers PRE and ATR. The autothermal reformer ATR operates with a flow 22 of enriched air or oxygen.

The synthesis gas, which contains H2, CO and CO2, undergoes a shift reaction in SHF and then removal of CO2 in CDR. The section SHF may comprise shift treatments at different temperatures. The section CDR operates

for example with chemical/physical washing of the gas using an aqueous amine solution.

The section CDR produces a CO2-depleted syngas 12 and a flow 13 of CO2 which may be sequestered or used for other process purposes, for example in order to produce urea.

Preferably the synthesis gas 12 has the following composition: 98% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

A part 14 of said CO2-depleted syngas 12 is used as fuel in a furnace in the front end, for example in a charge heater (AUX block). The remaining part 18 of synthesis gas is further treated in the methanator MET.

In the example, the fuel fraction 14 of synthesis gas, together with a tail gas 15 of the HRU section, feeds one or more users of the block AUX via the fuel line 16. Optionally a suitable quantity of natural gas 17 (trim gas) is added to the gas 16.

Nitrogen 18 from the air separation section ASU is added to the process fraction 18 of the synthesis gas, after it has passed inside the methanator (optional).

The gas thus obtained, together with a flow of hydrogen 20 recovered from the HRU section, feeds the synthesis section SYN. Said synthesis section produces ammonia 23 and a flow 21 of purging gas treated in the section HRU for recovery of the hydrogen contained inside it.

The separation section ASU produces, in addition to the nitrogen 19, also the flow 22 of enriched air or oxygen for the autothermal reformer ATR.

Fig. 2 shows a process according to a preferred mode of implementing the invention based on primary reforming and ATR.

The block SMR in Fig, 1 denotes the primary reformer (or steam reformer) plus

auxiliary apparatus, for example steam generators. The remaining symbols in Fig. 2 correspond to the symbols in Fig. 1 and therefore the description is not repeated.

Fig. 2 also shows an optional line 15a for recycling part of the tail gas 15 from the unit HRU for feeding the primary reformer SMR.

Fig. 3 shows an ATR-based process, similar to Fig. 1, but comprising a purification of the process fraction of the synthesis gas in a section PUR, which in this example comprises a PSA unit.

The fuel fraction 14 separated from the CO2-depleted synthesis gas 12 is divided into a first portion 14a used as fuel in a furnace in the front end, for example in the block AUX, and a second portion 14b exported as excess fuel. The remaining part 18 of synthesis gas is further treated in the PSA unit.

A portion 23 of the effluent of the PSA unit is (optionally) exported as excess fuel. Said portion 23 has a greater hydrogen purity than the gas portion 14b.

In the example shown in Fig, 3, the portion 14a of synthesis gas separated as fuel fraction, together with a tail gas 25 of the PSA unit, feeds one or more users of the block AUX via the fuel line 26.

Fig. 4 shows a process based on POX, comprising purification of the process fraction of the synthesis gas in a section PUR comprising dryer and LNW (liquid nitrogen wash).

In a similar manner to the embodiment shown in Fig. 3, also in this case the fuel fraction 14 separated from the CO2-depleted synthesis gas 12 is split into a first portion 14a used as fuel for example in the block AUX, and a second portion 14b exported as excess fuel. Said portion 14a, together with a tail gas 35 of the section PUR, feeds one or more users of the block AUX via the fuel line 36. Said tail gas 35 results from the combination of the tail gas of the LNW and of the dryer.

The process according to the invention allows to produce ammonia with emissions of CO2 of about 0.1 t/t compared to about 0.7 t/t in the prior art.

All the configurations illustrated may be the result of revamping of an ammonia plant with air-fed secondary reformer.

In one embodiment, the revamping procedure comprises essentially the following steps:

installing the ASU unit in order to generate the flow 22 of oxygen or enriched air;

modifying the secondary reformer in order to accept said flow 22 instead of air;

increasing the fraction of natural gas intended for the process and reducing the fraction of natural gas intended for fuel;

revamping the existing section for desulphurization of the natural gas so as to increase the capacity thereof owing to the greater process gas flowrate;

revamping the existing section CDR so as to increase the capacity thereof owing to the greater quantity of CO2 to be separated.

It can be understood that the revamping does not require costly modifications to the reformer, the exchangers and piping of the front end and the shift section. This is due to the fact that the volumetric flowrate of the gas through the front end does not increase, despite the generation of the additional gas fraction (fuel fraction).

Example:

The following Table 1 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced.

Table 1 compares the following options:

(1) Plant of the prior art with primary reformer and air-fed secondary reformer.

(2) Plant of the prior art, as per option (1), with capturing of the CO2 from the fumes of the primary reformer.

(3) Plant according to the invention, as per Fig. 1.

(4) Plant according to the invention, as per Fig. 2.

Table 1

Option		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
NH3 production	MTD	3000	3000	3000	3000
Net Natural Gas consumption based on gas LHV (FEED+FUEL-Steam exported e.g. to urea)	Gcal/t NH3	6.7	7.4	7.0	6.9
	Gcal/t NH3		+0.7	+0.3	+0.2
CO2 captured in process	MTD	3600	3600	5200	5100
CO2 to atmosphere (contained in flue gas)	MTD	2100	200	200	200
CO2 to atmosphere (contained in flue gas)	t/t NH3	0.7	0.1	0.1	0.1
Main Equipment size					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	100	145	140
ASU O2 capacity	%	n/a	n/a	100	60
Flowrate of front end (secondary output/ ATR)	%	100	100	120	97

The table shows that the process according to the invention (option 3) requires a front end suitable for producing also the gas fraction to be used as fuel in the furnaces; in fact the quantity of CO2 captured in the process amounts to 5200 MTD compared to 3600 for options (1) and (2), and the synthesis gas flowrate in the front end is about 20% more than Fig. 1 and 2. Despite this, the consumption of the plant is much less than that of option (2) (7.0 instead of 7.4 Gcal/MT) and is competitive with the plant without capturing according to

option (1). The total duty of the furnaces is only 75% of option (1).

In option (4) the energy consumption obtained is less than in option (3), i.e. equal to 6.9 Gcal/MT, and also the cost of the plant is less. This because, in option (4), the quantity of CO2 separated in the process is less than in option (3); the duty of the furnaces is greater than in (3), but is comparable with that of options (1) and (2); the oxygen consumption is markedly less than (3); the flowrate in the front end is markedly less than (3) and comparable with (1) and (2).

The examples show how the novel process is more efficient and competitive than the prior art.

The example also shows the advantage of modifying a plant operating as per option (1), preferably implementing option (4). In fact, in this case the duty of the furnaces and the flowrate of the gases remain substantially unvaried, while the CO2 emissions are reduced. The invention thus achieves the object of minimizing the CO2 emissions of a conventional plant without losing ammonia production.

The following Table 2 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced, which is self-sufficient from the point of view of the steam and electric power. The process comprises the consumption relating to the compression of the CO2 sequestered up to the pressure of 100 bar. For each process, the natural gas consumption and the CO2 emissions indicated also consider the superheated steam production in AUX for driving all the turbines, and the production of the electric power necessary for the process.

Table 2 compares the following options:

(1) Plant according to the invention, with SMR+ATR as per Fig. 2, in the following variants:

a. with the overall S/C ratio = 2.7, shift composed of HTS and LTS,

methanator, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 1a, but without trim fuel.

(2) Plant according to the invention, with pre-reformer + ATR as per Fig. 3, in the following variants:

a. with the overall S/C ratio = 2, shift composed of MTS and LTS, PSA, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 2a, without trim fuel, with the Selectoxo process downstream of SHF and upstream of CDR for converting the residual CO.

(3) Plant according to the invention, with POX, as per Fig. 4, in the variants:

a. with the overall S/C ratio = 2, shift composed of MTS and LTS, LNW dryer, trim fuel with flowrate corresponding to 10% of required duty of the furnace;

b. as for 2a, without trim fuel, with selective catalytic oxidation of CO (Selectoxo™ process) downstream of the shift reaction and upstream of the CO2 removal.

Table 2

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
Daily production of NH3, MTD	3000	3000	3000	3000	3000	3000
Daily throughput of sequestered CO2, MTD	5600	5800	5100	5300	5350	5600
Net consumption of natural gas (for Example 1a), dimensionless	100%	100%	93%	93%	95%	95%

CO2 emissions into atmosphere per unit of ammonia produced, t CO2/t NH3	0.15	0.075	0.17	0.10	0.15	0.05
Distribution of the CO2 emissions						
- trim fuel	50%	zero	20%	zero	20%	zero
- CH4 slip in the process gas	15%	29%	40%	79%	30%	63%
- CO slip in the process gas	34%	69%	39%	19%	49%	34%
- CO2 slip in the process gas	1%	2%	1%	2%	1%	3%

In Table 2:

"Trim fuel" as defined in the patent;

"CH4 slip in the process gas" is the residual methane content of the synthesis gas produced in the front end (i.e. in SMR + ATR in option 1, in the pre-reformer + ATR in option 2, POX in option 3), quantified upstream of optional methanation.

"CO slip in the process gas" is the residual carbon monoxide content of the synthesis gas downstream of the shift section;

"CO2 slip in the process gas" is the residual carbon dioxide content of the synthesis gas downstream of the CO2 removal section;

Several comments may be made in view of Table 2:

- In the case of SMR+ATR in option 1a, the trim fuel provides the greatest percentage of the CO2 emissions; avoiding the trim fuel by exporting surplus fuel enables the emissions to be significantly reduced to less than 0.1

t/t, as shown in the Table for option 1b; at the same time, the quantity of sequestered CO2 increases from 5600 to 5800 MTD.

- In the case of SMR+ATR, the CO slip in the process gas provides the second greatest percentage of the CO2 emissions in option 1a, and provides the greatest percentage in option 1b; application of the Selectoxo process to option 1a or 1b would significantly reduce the CO2 emissions; the CH4 slip in the process gas and the CO2 slip in the process gas provides a smaller percentage of the CO2 emissions.

- The overall energy consumption of the options based on ATR and POX + purification (2 and 3) is decidedly lower than that of the options based on SMR + ATR (1a and 1b); this is mainly due to the synthesis gas purification (which improves the efficiency of the synthesis section and avoids the purge); the quantity of CO2 sequestered in these options (2a, 3a; or 2b, 3b) is consequently less than in options 1a or 1b.

- The emissions due to the use of the trim fuel in options 2a (ATR) and 3a are of about 20% of the total emissions, much less than in option 1a, by way of confirmation of the fact that the heat required by the furnace in these two options is much less than in option 1a.

- In the embodiments with ATR or POX, the residual CO and CH4 are of higher relevance owing to the lower S/C ratio at which ATR and POX operate compared to SMR+ATR; POX operates at a higher temperature than ATR, which results in a smaller residual amount of CH4, but in a greater residual amount of CO.

- In both the options 2b and 3b, the improvement achieved by selective oxidation of CO, in order to reduce the CO slip, and by avoiding trim fuel, is evident.

- It should be noted that both POX and ATR achieve very low emissions - as low as 0.05 for POX and 0.1 for ATR - comparable with those achieved by

SMR+ATR, but with lower energy consumption, and therefore preferable.

The above example shows how the invention is able to achieve extremely low CO2 emission levels, corresponding to almost total capture (>98%), while maintaining competitive energy consumption levels.

5

CLAIMS

1) Process for synthesis of ammonia from natural gas, comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas (11) containing hydrogen, CO and CO2, in a conversion section;

a treatment of said synthesis gas (11) comprising at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas (12) and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas,

characterized by:

separation of a part (14) of said CO2-depleted synthesis gas (12) as fuel fraction, wherein said fuel fraction (14) is fed as fuel to at least one furnace.

2) Process according to claim 1, wherein said separation of the fuel fraction comprises the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia, optionally after further purification.

3) Process according to claim 1 or 2, wherein said fuel fraction (14) is comprised between 1% and 40% of the total amount of said CO2-depleted syngas (12), preferably between 10% and 30%.

4) Process according to any one of the preceding claims, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

5) Process according to any one of the preceding claims, wherein said CO2-depleted syngas (12) contains no more than 1000 ppm by volume of CO2.

6) Process according to any one of the preceding claims, wherein said enriched air contains at least 50% of oxygen, preferably at least 90% oxygen.

7) Process according to any one of the preceding claims, wherein said fuel fraction (14) of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

8) Process according to any one of the preceding claims, wherein: a purge gas (21) of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in it, obtaining a hydrogen-rich gas (20) and a tail gas (15) containing methane; at least part (15a) of said tail gas (15) is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

9) Process according to any one of the preceding claims, wherein: a part of said CO2-depleted syngas (12) is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, preferably all of it, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

10) Process according to any one of the preceding claims, also comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas (12), optionally after heating it.

11) Process according to any one of the preceding claims, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0, preferably

greater than 2.4 and more preferably greater than 2.7.

12) Process according to any one of the preceding claims, wherein

said synthesis gas fuel fraction (14) forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

13) Process according to any one of the preceding claims, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

14) Process according to any one of the preceding claims, wherein:

the conversion of the natural gas charge into synthesis gas comprises a step of autothermal reforming, optionally with pre-reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

15) Process according to any one of the preceding claims, wherein the conversion of the natural gas into synthesis gas comprises: primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

16) Process according to any one of the preceding claims, wherein the CO2 emissions are less than 0.5 tonnes of CO2 emitted per tonne of ammonia

produced.

17) Method for revamping a plant for the synthesis of ammonia from natural gas or ammonia/urea plant, wherein

the plant comprises a reforming section which includes a primary steam reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by means of a shift reaction of carbon monoxide into carbon dioxide, decarbonation and optionally methanation.

and the revamping method comprises at least:

providing a flow (22) of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part (14) of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction (14) of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

18) Method for revamping according to claim 17 comprising: installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

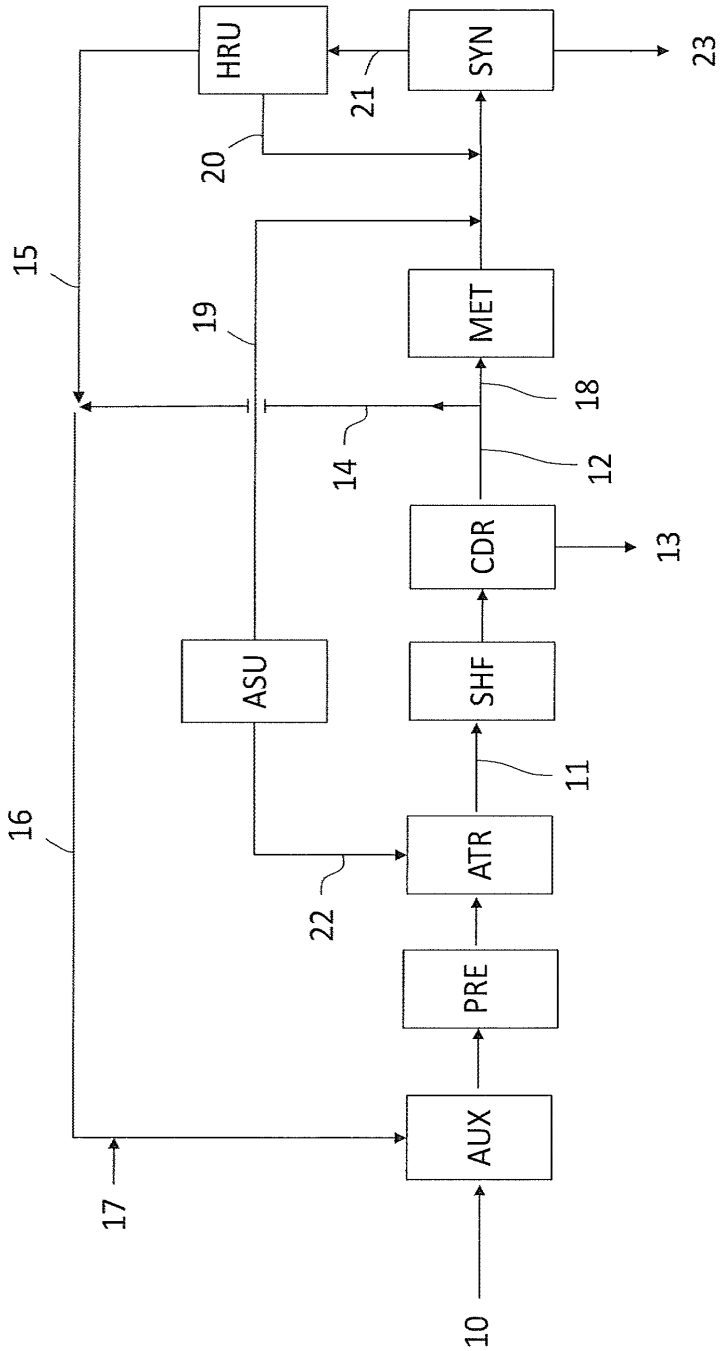

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FIG. 1

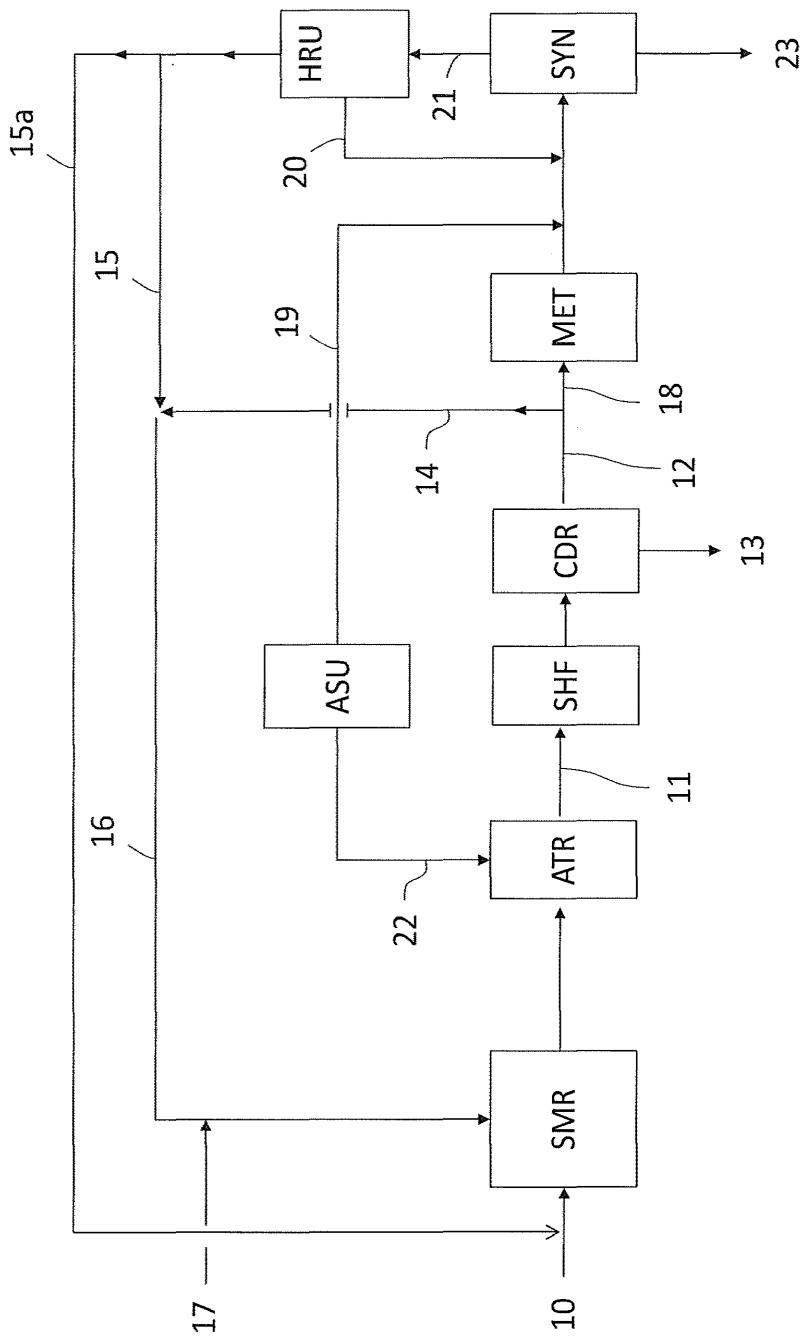

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FIG. 2

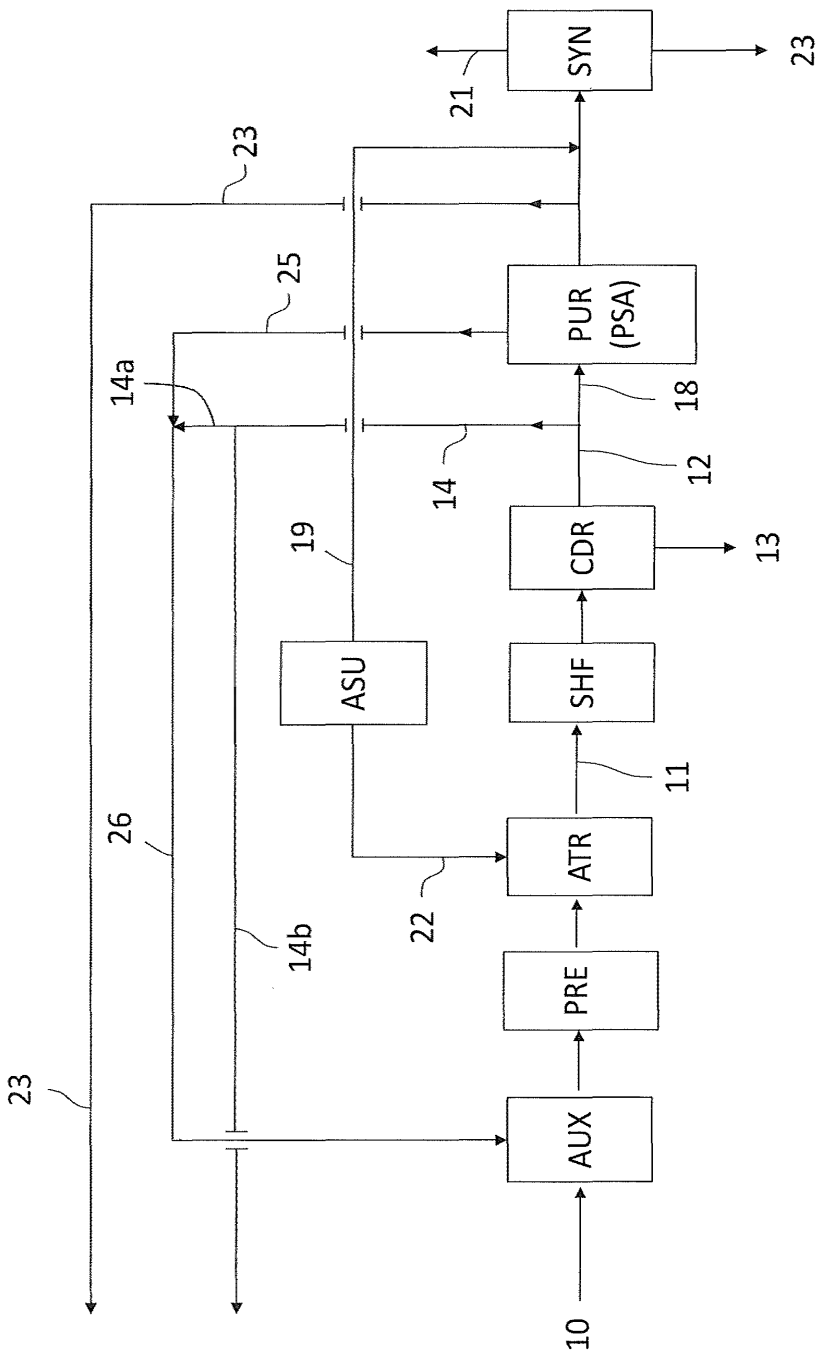

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AUX
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FIG. 3

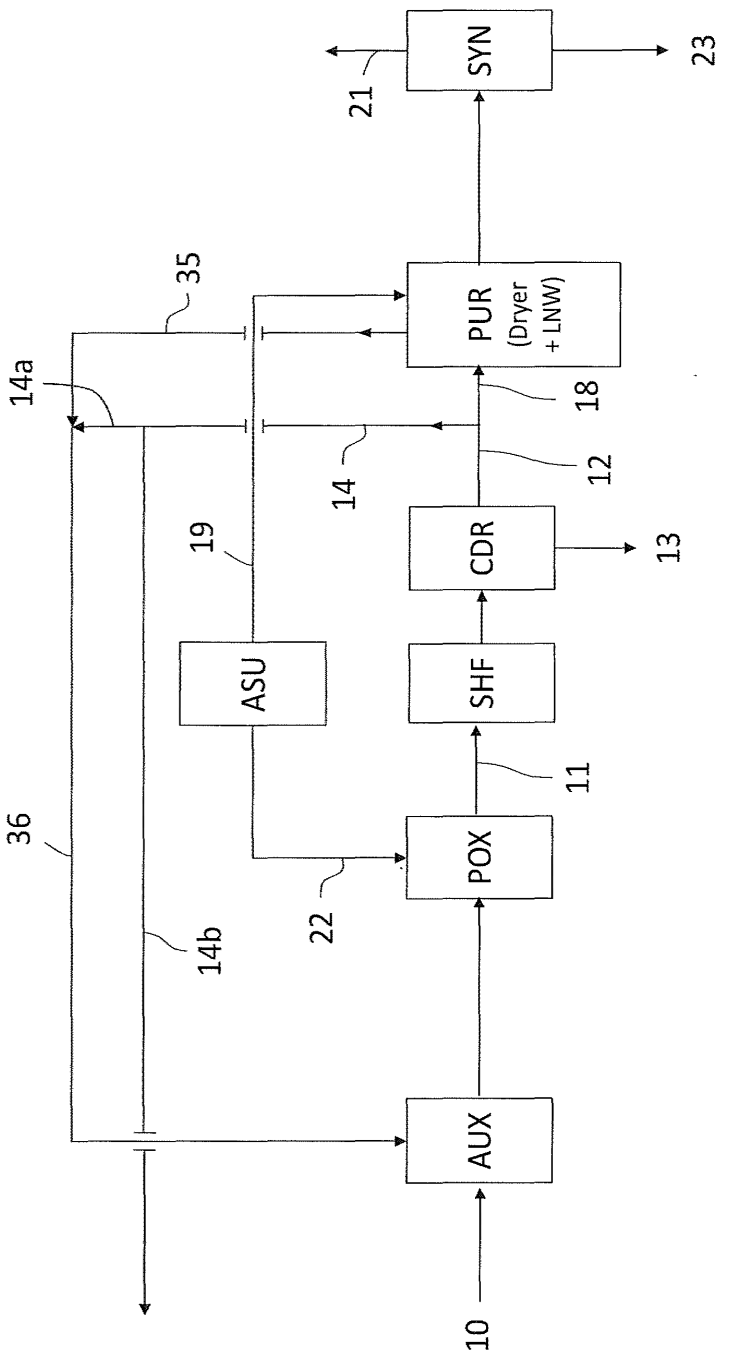

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PUR
(Dryer
+ LNW)
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CDR
19
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ASU
SHF
11
36
POX
22
14b
AUX
10

FIG. 4

AMC121WUS

UNITED STATES PATENT **Attorney Docket No. _____**
Form US

COMBINED DECLARATION and ASSIGNMENT
(Utility, Design, National Stage of PCT)

TITLE OF INVENTION: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

As a below named inventor, I hereby declare that:

SPECIFICATION IDENTIFICATION

This declaration and assignment is directed to:

(complete (a), (b), or (c))

(a) [ ] The attached application (United States Application No. _____, filed on _____);

(b) [ ] Previously filed United States Application No. _____, filed on _____; or

(c) [X] PCT International Application No. PCT/EP2018/052358, filed on 31 January 2018 (nationalized as United States Application No. _____, filed on _____).

I hereby authorize the patent attorneys and/or patent agents of Dorsey & Whitney LLP to insert the above Application No(s). and filing date(s) when known.

DECLARATION AND ACKNOWLEDGEMENT

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

I believe that I am the original inventor or an original joint inventor of a claimed invention in the above-identified application.

I hereby state that I have reviewed and understand the contents of the above-identified application, including the claim(s).

I acknowledge the duty to disclose all information which is material to patentability as defined in 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. § 1001 by fine or imprisonment of not more than five (5) years, or both.

ASSIGNMENT

The Assignee, Casale SA, having a principal place of business at Via Pocobelli 6, Lugano, Switzerland 6900, desires to secure the entire right, title and interest in the above-identified application and in the invention disclosed therein.

In consideration of One Dollar ($1.00) and other good and valuable consideration paid to me by the Assignee, the receipt and sufficiency of which is hereby acknowledged, I HEREBY ASSIGN TO THE ASSIGNEE:

> The entire right, title and interest in the above-identified application and in the invention disclosed therein and in all divisions, continuations and continuations-in-part of said application and in all corresponding applications filed in countries foreign to the United States and in all patents issuing thereon in the United States and foreign countries and in all reissues or extensions of patents granted thereon.
>
> The right to file foreign patent applications on said invention in its own name, wherever such right may be legally exercised, including the right to claim the priority to or the benefit of the above-identified application including under all applicable treaties and conventions.

I hereby authorize and request the United States Commissioner of Patents and Trademarks, and such Patent Office officials in foreign countries as are duly authorized by their patent laws to issue patents, to issue any and all patents on said invention to the Assignee as the owner of the entire interest, for the sole use and behoof of the said Assignee, its successors, assigns and legal representatives.

I hereby agree, without further consideration and without expense, to sign all lawful papers and to perform all other lawful acts which the Assignee may request of me to make this Assignment fully effective, including, by way of example but not of limitation, the following:

> Prompt execution of all original, divisional, continuation, continuation-in-part, substitute, reissue, and other United States and foreign patent applications on the invention, and all lawful documents requested by the Assignee to further the prosecution of any of such patent applications.

> Cooperation to the best of my ability in: (1) proceedings relating to nullification, reissue, extension, post grant, inter partes, derivation, supplemental examination, and infringement involving the invention; (2) execution of all lawful documents involving the invention; and (3) the production of evidence involving the invention.

This assignment and agreement shall be binding upon my heirs and legal representatives.

SIGNATURE(S)

Full name of sole or first inventor

Francesco		Baratto
(GIVEN NAME)	*(MIDDLE INITIAL OR NAME)*	*FAMILY (OR LAST NAME)*

Signature [signature] Date 28 August 2019

Full name of second joint inventor, if any

Raffaele		Ostuni
(GIVEN NAME)	*(MIDDLE INITIAL OR NAME)*	*FAMILY (OR LAST NAME)*

Signature [signature] Date 28 August 2019

Electronic Acknowledgement Receipt	
EFS ID:	37293237
Application Number:	16485695
International Application Number:	
Confirmation Number:	3128
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Customer Number:	116407
Filer:	Marcus S. Simon/Angela Staschke
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	28336WOUS01_495230-44
Receipt Date:	27-SEP-2019
Filing Date:	
Time Stamp:	09:41:58
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Oath or Declaration filed	283386WOUS01_495230_44_Combined_Declaration_Assignment.pdf	254302 0c2318cef9c0adf069963b9768ce5c8808ade5bb	no	3

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Total Files Size (in bytes):	254302

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

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www.uspto.gov

U.S. APPLICATION NO.	FIRST NAMED INVENTOR	ATTY. DOCKET NO.
16/485,695	Francesco Baratto	28336WOUS01_495230-44

116407
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

INTERNATIONAL APPLICATION NO.	
PCT/EP2018/052358	
I.A. FILING DATE	PRIORITY DATE
01/31/2018	02/15/2017

CONFIRMATION NO. 3128
371 ACCEPTANCE LETTER

OC000000112544382

Date Mailed: 11/13/2019

NOTICE OF ACCEPTANCE OF APPLICATION UNDER 35 U.S.C 371 AND 37 CFR 1.495

The applicant is hereby advised that the United States Patent and Trademark Office, in its capacity as a Designated / Elected Office (37 CFR 1.495), has ACCEPTED the above identified international application for national patentability examination in the United States Patent and Trademark Office.

The United States Application Number assigned to the application is shown above. A Filing Receipt will be issued for the present application in due course. **THE DATE APPEARING ON THE FILING RECEIPT AS THE "FILING DATE or 371(c) DATE" IS THE DATE ON WHICH THE LAST OF THE 35 U.S.C. 371 (c)(1) and (c)(2) REQUIREMENTS HAS BEEN RECEIVED IN THE OFFICE. THIS DATE IS SHOWN BELOW.** The filing date of the above identified application is the international filing date of the international application (Article 11(3) and 35 U.S.C. 363)

08/13/2019
DATE OF RECEIPT OF 35 U.S.C.
371(c)(1) and (c)(2) REQUIREMENTS

The following items have been received:

- Indication of Small Entity Status
- Copy of the International Application filed on 08/13/2019
- Copy of the International Search Report filed on 08/13/2019
- Preliminary Amendments filed on 08/13/2019
- Information Disclosure Statements filed on 08/13/2019
- Inventor's Oath or Declaration filed on 09/27/2019
- U.S. Basic National Fees filed on 08/13/2019
- Assignment filed on 09/27/2019
- Authorize Access to Search Results filed on 08/13/2019
- Priority Documents filed on 08/13/2019
- Power of Attorney filed on 08/13/2019
- Authorization to Permit Access filed on 08/13/2019
- Application Data Sheet (37 CFR 1.76) filed on 08/13/2019

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

TONI M HOOD

Telephone: (571) 272-3654

FORM PCT/DO/EO/903 (371 Acceptance Notice)

UNITED STATES PATENT AND TRADEMARK OFFICE

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

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
16/485,695	08/13/2019		1010	28336WOUS01_495230-44	23	2

CONFIRMATION NO. 3128

FILING RECEIPT

116407
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176



Date Mailed: 11/13/2019

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

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

Inventor(s)

Francesco Baratto, Como, ITALY;
Raffaele Ostuni, Lugano, SWITZERLAND;

Applicant(s)

CASALE SA, Lugano, SWITZERLAND;

Power of Attorney: The patent practitioners associated with Customer Number 116407

Domestic Priority data as claimed by applicant

This application is a 371 of PCT/EP2018/052358 01/31/2018

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)
EUROPEAN PATENT OFFICE (EPO) 17195305.2 10/06/2017
EUROPEAN PATENT OFFICE (EPO) 17156256.4 02/15/2017

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

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

If Required, Foreign Filing License Granted: 11/09/2019

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 16/485,695**

Projected Publication Date: 02/20/2020

Non-Publication Request: No

Early Publication Request: No
** **SMALL ENTITY** **
Title

PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

Preliminary Class

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

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

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

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

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

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

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

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Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 16/485,695

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	150		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	260		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	380		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	23 minus 20 =	* 3	x 50 =	150	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 minus 3 =	*	x 230 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	940		TOTAL	

APPLICATION AS AMENDED - PART II

AMENDMENT A

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

AMENDMENT B

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

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

MULTIPLE DEPENDENT CLAIM FEE CALCULATION SHEET

Substitute for Form PTO-1360
(For use with Form PTO/SB/06)

Application Number	Filing Date
16485695	

Applicant(s) Francesco Baratto

* May be used for additional claims or amendments

CLAIMS	AS FILED		AFTER FIRST AMENDMENT		AFTER SECOND AMENDMENT	
	Indep	Depend	Indep	Depend	Indep	Depend
1			1			
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Total Indep	0		2		0	
Total Depend	0	↵	21	↵	0	↵
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To: simon.marcus@dorsey.com,ip.docket.slc@dorsey.com,ip.patent.sl@dorsey.com
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Application	Document	Mailroom Date	Attorney Docket No.
16485695	M903	11/13/2019	28336WOUS01_495230-44
	APP.FILE.REC	11/13/2019	28336WOUS01_495230-44

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/485,695	08/13/2019	Francesco Baratto	28336WOUS01_495230-44

CONFIRMATION NO. 3128

116407
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Salt Lake City, UT 84111-2176

PUBLICATION NOTICE



Title:PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

Publication No.US-2020-0055738-A1
Publication Date:02/20/2020

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

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Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

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Application	Document	Mailroom Date	Attorney Docket No.
16485695	NTC.PUB	02/20/2020	28336WOUS01_495230-44

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/485,695	08/13/2019	Francesco Baratto	28336WOUS01_495230-44	3128

116407 7590 04/28/2021

Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER	
PARSA, JAFAR F	

ART UNIT	PAPER NUMBER
1622	

NOTIFICATION DATE	DELIVERY MODE
04/28/2021	ELECTRONIC

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

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

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

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ip.patent.sl@dorsey.com
simon.marcus@dorsey.com

Office Action Summary	**Application No.** 16/485,695	**Applicant(s)** Baratto et al.	
	Examiner JAFAR F PARSA	**Art Unit** 1622	**AIA (FITF) Status** Yes

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

Period for Reply

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

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

Status

1)☑ Responsive to communication(s) filed on 08/13/2019.

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

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

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

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

Disposition of Claims*

5) ☑ Claim(s) 19-41 is/are pending in the application.

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

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 19-41 is/are rejected.

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

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

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

Application Papers

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

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

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

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

Priority under 35 U.S.C. § 119

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

Certified copies:

a)☑ All b)☐ Some** c)☐ None of the:

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

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

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

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

Attachment(s)

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

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date 1.

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

4) ☐ Other: _____.

DETAILED ACTION

Notice of Pre-AIA or AIA Status

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

Claim Rejections - 35 USC § 103

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

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

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

The factual inquiries for establishing a background for determining obviousness under 35 U.S.C. 103 are summarized as follows:

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

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

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

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

Claims 19-41 are rejected under 35 U.S.C. 103 as being unpatentable over Reddy et al (US 2004/0234426) in view of Ostuni et al (US 2016/0115017 A1).

Applicants' claimed invention is directed to a process for synthesis of ammonia from natural gas, the process comprising: conversion of a charge of desulfurized natural gas and steam, with oxygen- enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO_2, in a conversion section; treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO_2, and subsequent separation of $C0_2$ from the gas, thus obtaining a CO_2-depleted synthesis gas and a $C0_2$-rich gaseous flow containing the CO_2 separated from the gas; separation of a part of said CO_2-depleted synthesis gas as fuel fraction, wherein said fuel fraction is fed as fuel to at least one furnace and wherein said separation of the fuel fraction includes the split of said CO_2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.

Reddy teaches a method for making ammonia comprising reforming In the exemplary configuration of FIG. 2, plant 200 includes primary and secondary reformers 210 and 220, respectively, in which the natural gas feed 202 is converted using steam 204, stoichiometric amounts of process air 205A, additional process air 205B, and appropriate catalysts/reaction conditions to produce reformer effluent 226 predominantly comprising carbon monoxide, hydrogen, and nitrogen. The term "stoichiometric amounts of process air" refers to the quantity of process air that will provide a molar ratio of hydrogen to nitrogen of about 3.0 after shift conversion and optionally after the

methanator in the syngas, natural gas using a gas comprising 90% oxygen from an ASU. The syngas obtained is shift converted and then CO_2 is removed. The CO_2 depleted syngas is treated in a coldbox whereby two streams are obtained. One stream is sent to the ammonia converter and the other stream is used as fuel in the primary reformer. Before the CO_2 depleted syngas is treated in a coldbox it is treated in a methanator. Therefore, the depleted syngas will inevitably have an amount of $C0_2$ < l000 ppm. The tail gas means CO_2 depleted syngas used as fuel gas can be compressed followed by expansion. Reddy further disclosed that existing ammonia plants can be revamped using the means disclosed in Reddy, namely an ASU and a coldbox with which two streams are obtained, one which is sent to the ammonia converter and the other which is used as fuel in the primary reformer. See paragraphs 0023-0027, 0032, 0034 and Figures 2 and 3.

Furthermore, Reddy teaches carbon dioxide removal from the gas stream may be achieved using various methods known in the art, and all of the known methods and configurations are contemplated suitable for use herein. Consequently, suitable carbon dioxide removal may include use of physical or chemical solvents, or membranes. Moreover, contemplated acid gas removal also includes removal of compounds other than carbon dioxide, and contemplated compounds especially include hydrogen sulfide and other sulfur containing compounds. See paragraph 0044.

Reddy teaches that the methanator effluent 262 is fed to coldbox 270 that is operated under conditions to separate the methanator effluent 262 into a fuel gas portion 272 predominantly comprising methane, hydrogen, and nitrogen, and a purified and cooled syngas with a nitrogen to hydrogen ratio of about 3:1. The fuel gas is

preferably fed into the burner of the primary reformer 210, while the cooled synthesis gas is compressed in syngas compressor 280 before entering the synthesis loop 290. Synthesis loop 290 produces ammonia product 292 and purge gas 294, which is optionally combined with fuel gas 272 for combustion in the primary reformer 210. See paragraph 0025.

Reddy teaches that the first portion of methanator effluent 662A is fed to the PSA 685 that separates the methanator effluent 662A into a hydrogen rich stream 662A' and a waste stream 662A", predominantly comprising methane, hydrogen, and nitrogen. A second portion of methanator effluent 662B is fed directly to the syngas compressor 680, that also compresses hydrogen rich stream 662A' to form a compressed syngas having a molar ratio of hydrogen to nitrogen of about 3.0. The waste gas is preferably combined with the purge gas from the synloop 690 to combined waste gas stream 672 and fed into the burner of primary reformer 610, while the synthesis loop 690 produces ammonia product 692. See paragraph 0040.

The instant claims differ from Reddy in using desulfurized natural gas into a synthesis gas, secondly Reddy is silent with respect to the concentration of CO_2-depleted gas as a fuel and finally, the overall ratio of steam/carbon ratio in conversion step. However, Ostuni in a process for producing ammonia teaches that the hydrocarbon feedstock is preferably a desulphurized natural gas to produce ammonia syngas from the reforming of a desulphurized natural gas, by means of a primary steam reforming and subsequent secondary reforming of the effluent. See paragraphs 0021 and 0003. Furthermore, Ostuni teaches a method of revamping a front-end of an ammonia plant, wherein said front-end comprises a primary reforming stage and an air-

fired secondary reforming stage, and also comprises a high-temperature shift converter with an iron based catalyst and running at a temperature greater than 320 C, and wherein the original front-end operates with a global steam-to-carbon ratio of 2.6 or greater. The method is characterized in that the secondary reforming stage is modified to operate with oxygen or oxygen-enriched air, with at least 50% oxygen, as oxidant stream, instead of air, and in that the amount of the hydrocarbon feedstock and the amount of steam fed to the front-end are regulated in such a way that the global steam-to-carbon ratio of the revamped front-end is 2.6 or less. See paragraph 0034, 0041 and claim 10.

It would therefore have been obvious to one of ordinary skilled in the art before the effective filing date of the claimed invention to incorporate the teachings of the Ostuni in Reddy's process with an optimum amount of CO2-depleted gas as a fuel to the reformer or furnace, further to reduce said SC ratio, in order to reduce the flow rate and hence the size of the equipment, and also to reduce the energy consumption.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JAFAR F PARSA whose telephone number is (571)272-0643. The examiner can normally be reached on M-F 10:00 AM-6:30PM.

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

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Brandon J Fetterolf can be reached on 571-272-2919. The fax phone

number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see https://ppair-my.uspto.gov/pair/PrivatePair. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/JAFAR F PARSA/
Primary Examiner, Art Unit 1622

Notice of References Cited	Application/Control No. 16/485,695	Applicant(s)/Patent Under Reexamination Baratto et al.	
	Examiner JAFAR F PARSA	Art Unit 1622	Page 1 of 2

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-20160115017-A1	04-2016	Ostuni; Raffaele	C01B3/48	252/374
	B					
	C					
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FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
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	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
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Notice of References Cited	Application/Control No. 16/485,695	Applicant(s)/Patent Under Reexamination Baratto et al.	
	Examiner JAFAR F PARSA	Art Unit 1622	Page 2 of 2

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
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Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	Art Unit
	JAFAR F PARSA	1622

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

CLAIMS

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

CLAIM		DATE								
Final	Original	04/24/2021								
	19	✓								
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	41	✓								

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	Art Unit
	JAFAR F PARSA	1622

CPC - Searched*		
Symbol	Date	Examiner
C01C 1/04	04/24/2021	JP
C01B 3/025, 3/48, 2203/0244, 2203/0283, 2203/042, 2203/0445, 2203/068, 2203/0827, 2203/86	04/24/2021	JP

CPC Combination Sets - Searched*		
Symbol	Date	Examiner

US Classification - Searched*			
Class	Subclass	Date	Examiner

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

Search Notes		
Search Notes	Date	Examiner
WEST	04/24/2021	JP
INVENTOR NAME SEARCH (PALM)	04/24/2021	JP

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

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CONFIRMATION NO. 3128

SERIAL NUMBER	FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
16/485,695	08/13/2019 RULE	423	1622	28336WOUS01_495230-44

APPLICANTS
CASALE SA, Lugano, SWITZERLAND;

INVENTORS
Francesco Baratto, Como, ITALY;
Raffaele Ostuni, Lugano, SWITZERLAND;

**** CONTINUING DATA ***************************
This application is a 371 of PCT/EP2018/052358 01/31/2018

**** FOREIGN APPLICATIONS ***************************
EUROPEAN PATENT OFFICE (EPO) 17195305.2 10/06/2017
EUROPEAN PATENT OFFICE (EPO) 17156256.4 02/15/2017

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11/09/2019

Foreign Priority claimed ☑ Yes ☐ No 35 USC 119(a-d) conditions met ☑ Yes ☐ No Verified and Acknowledged /JAFAR F PARSA/ Examiner's Signature	☐ Met after Allowance Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
		ITALY	4	23	2

ADDRESS
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176
UNITED STATES

TITLE
PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

FILING FEE RECEIVED		
1010	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

PALM INTRANET

Day : Saturday
Date: 4/24/2021
Time: 12:47:12

Inventor Name Search Result

Your Search was:

Last Name = BARATTO
First Name = FRANCESCO

Application#	Patent#	PG Pub#	Status	Date Filed	Title	Examiner Name	Inventor Name
12415556	8039512	20090264542	150	03/31/2009	PROCESS AND PLANT FOR SUBSTITUTE NATURAL GAS	PARSA,JAFAR	BARATTO, FRANCESCO
13233892	Not Issued	20120017508	161	09/15/2011	Process and Plant for Substitute Natural Gas	LEUNG,JENNIFER	BARATTO, FRANCESCO
13660724	Not Issued	20130046031	161	10/25/2012	Process and Plant for Substitute Natural Gas	LEUNG,JENNIFER	BARATTO, FRANCESCO
13805916	10087074	20130101490	150	12/18/2012	PROCESS FOR PRODUCING AMMONIA SYNTHESIS GAS	CALL,DOUGLAS	BARATTO, FRANCESCO
14790273	Not Issued	20150307797	161	07/02/2015	PROCESS AND PLANT FOR SUBSTITUTE NATURAL GAS	LEUNG,JENNIFER	BARATTO, FRANCESCO
16142292	Not Issued	20190023565	61	09/26/2018	PROCESS FOR PRODUCING AMMONIA SYNTHESIS GAS	CALL,DOUGLAS	BARATTO, FRANCESCO
16485695	Not Issued	20200055738	30	08/13/2019	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	PARSA,JAFAR	BARATTO, FRANCESCO
16722889	Not Issued	0	41	06/15/2020	MULTI-BED CATALYTIC CONVERTER	SEIFU,LESSANEWORK	BARATTO, FRANCESCO
17053152	Not Issued		19	01/01/0001	A PROCESS FOR NITRIC ACID PRODUCTION	.	BARATTO, FRANCESCO

Inventor Search Completed: No Records to Display.

Search Another: Inventor **Last Name** BARATTO **First Name** FRANCESCO Search

To Go BACK Use BACK Button on Your BROWSER Tool Bar
Back to PALM | ASSIGNMENT | OASIS | Home page

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Field

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	TBD
	Filing Date	August 13, 2019
	First Named Inventor	Francesco Baratto
	Art Unit	TBD
	Examiner Name	TBD
	Attorney Docket Number	283386WOUS01_495230-44

U.S.PATENT APPLICATION PUBLICATIONS

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
/J.P/		20040234426	A1	2004-11-25	Reddy et al.	
/J.P/		20140248205	A1	2014-09-04	Allam	
/J.P/		20150031916	A1	2015-01-29	Kiss	

FOREIGN PATENT DOCUMENTS

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2]	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages, Columns, Lines where Relevant Passages or Relevant Figures Appear	T[5]
/J.P/		2010018550	WO	A1	2010-02-18	Vakil et al.		

NON-PATENT LITERATURE DOCUMENTS

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
/J.P/		International Preliminary Report on Patentability for International Application No. PCT/EP2018/052358 completed May 10, 2019	
/J.P/		International Search Report from International Application No. PCT/EP2018/052358 mailed July 31, 2018	

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Field

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
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	First Named Inventor	Francesco Baratto
	Art Unit	TBD
	Examiner Name	TBD
	Attorney Docket Number	283386WOUS01_495230-44

EXAMINER SIGNATURE			
Examiner Signature	/JAFAR F PARSA/	Date Considered	04/24/2021

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document.
[4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Field

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	TBD
	Filing Date	August 13, 2019
	First Named Inventor	Francesco Baratto
	Art Unit	TBD
	Examiner Name	TBD
	Attorney Docket Number	283386WOUS01_495230-44

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e) (1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e) (2).

☐ See attached certification statement.

☐ Fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☒ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Marcus S. Simon, Reg.# 50258/	Date (YYYY-MM-DD)	2019-08-13
Name/Print	Marcus S Simon	Registration Number	50258

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

WEST Search History

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DB=PGPB,USPT,USOC,EPAB,JPAB,DWPI,TDBD,FPRS; THES=ASSIGNEE; PLUR=YES; OP=ADJ			
☐	L8	L7 AND (CARBON DIOXIDE OR "{CO.SUB.2}") WITH (SEPARAT$3 OR REMOV$3 OR DEPLET$2) SAME FUEL WITH (FURNACE OR REFORM$3)	21
☐	L7	L6 AND SHIFT NEAR1 REACT$3	74
☐	L6	L4 AND (NATURAL GAS OR METHANE) WITH STEAM WITH (OXYGEN OR AIR) WITH (SYNGAS OR SYNTHESIS GAS) WITH AMMONIA	229
☐	L5	L4 AND (NATURAL GAS OR METHANE) WITH STEAM WITH (OXYGEN OR AIR) WITH (SYNGAS OR SYNTHESIS GAS) WITH AMMONIA	229
☐	L4	L3 OR L2 OR L1	1942661
☐	L3	C07C.CPCL.	1461054
☐	L2	C01B.CPCL.	491191
☐	L1	C01C.CPCL.	30725

END OF SEARCH HISTORY

Topsoe, Inc. – EX1002
Page 307 of 356

To: simon.marcus@dorsey.com,ip.docket.slc@dorsey.com,ip.patent.sl@dorsey.com
From: PAIR_eOfficeAction@uspto.gov
Cc: PAIR_eOfficeAction@uspto.gov
Subject: Private PAIR Correspondence Notification for Customer Number 116407

Apr 28, 2021 03:54:16 AM

Dear PAIR Customer:

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UNITED STATES

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Application	Document	Mailroom Date	Attorney Docket No.
16485695	CTNF	04/28/2021	28336WOUS01_495230-44
	892	04/28/2021	28336WOUS01_495230-44
	1449	04/28/2021	28336WOUS01_495230-44

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Thank you for prompt attention to this notice,

UNITED STATES PATENT AND TRADEMARK OFFICE

PATENT APPLICATION INFORMATION RETRIEVAL SYSTEM

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of		)
	Francesco Baratto, *et al.*	)
Serial No.:	16/485,695	) Art Unit 1622
Filed:	Concurrently Herewith	)
Confirmation No.:	3128	)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
Examiner:	Jafar F. Parsa	)
Customer No.:	116407	)

RESPONSE "A" UNDER 37 C.F.R. § 1.111

VIA *e*FILE AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In response to the Non-Final Office Action dated April 28, 2021, please consider the following remarks/arguments:

Listing of the Claims begins on page 2 of this paper.

Remarks/Arguments begin on page 6 of this paper.

LISTING OF THE CLAIMS

The listing of claims will replace all prior versions and listings of claims in the application:

1-18. (Canceled)

19. (Previously Presented) A process for synthesis of ammonia from natural gas, the process comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO2, in a conversion section;

treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

separation of a part of said CO2-depleted synthesis gas as fuel fraction, wherein said fuel fraction is fed as fuel to at least one furnace and wherein said separation of the fuel fraction includes the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.

20. (Previously Presented) The process of claim 19, wherein the first stream forms the fuel fraction and the second stream is the process gas intended for the synthesis of ammonia after further purification.

21. (Previously Presented) The process of claim 19, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.

22. (Previously Presented) The process of claim 19, wherein said fuel fraction is between 10% and 30% of the total amount of said CO2-depleted syngas.

23. (Previously Presented) The process of claim 19, further comprising a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas.

24. (Previously Presented) The process of claim 23, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

25. (Previously Presented) The process of claim 19, wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.

26. (Previously Presented) The process of claim 19, wherein said enriched air contains at least 50% oxygen.

27. (Previously Presented) The process of claim 19, wherein said enriched air contains at least 90% oxygen.

28. (Previously Presented) The process of claim 19, wherein said fuel fraction of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; or one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

29. (Previously Presented) The process of claim 19, wherein: a purge gas of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in the purge gas, obtaining a hydrogen-rich gas and a tail gas containing methane; at least part of said tail gas is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

30. (Previously Presented) The process of claim 19, wherein: a part of said CO2-depleted syngas is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

31. (Previously Presented) The process of claim 19, further comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas, after heating the CO2-depleted syngas.

32. (Previously Presented) The process of claim 19, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0.

33. (Previously Presented) The process of claim 19, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.

34. (Previously Presented) The process of claim 19, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.

35. (Previously Presented) The process of claim 19, wherein

said synthesis gas fuel fraction forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

36. (Previously Presented) The process of claim 19, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process; and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

37. (Previously Presented) The process of claim 19, wherein:

the conversion of the natural gas charge into synthesis gas includes a step of autothermal reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

38. (Previously Presented) The process of claim 19, wherein the conversion of the natural gas into synthesis gas includes primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

39. (Previously Presented) A method for revamping a plant for synthesis of ammonia from natural gas or ammonia/urea plant, wherein the plant includes a reforming section that includes a primary steam reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation; the method comprising:

providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

40. (Previously Presented) The method of claim 39, further comprising installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

41. (Previously Presented) The method of claim 39, wherein the section for treatment of the synthesis gas by the shift reaction of carbon monoxide includes methanation.

REMARKS

A. BACKGROUND

This paper is in response to the Office Action dated April 28, 2021 by the U.S. Patent and Trademark Office ("PTO"). Claims 19-41 were pending and rejected in view of cited art.[1] No claims are canceled, amended, or are added. Claims 19-41 are still pending in view of the above amendments.

Reconsideration of the application is respectfully requested in view of the following remarks. For the Examiner's convenience and reference, Applicant's remarks are presented in the order in which the corresponding issues were raised in the Office Action.

Please note that the following remarks are not intended to be an exhaustive enumeration of the distinctions between any cited references and the claimed subject matter. Rather, the distinctions identified and discussed below are presented solely by way of example to illustrate some of the differences between the claimed subject matter and the cited references. In addition, Applicant requests that the Examiner carefully review any references discussed below to ensure that Applicant's understanding and discussion of the cited references, if any, are consistent with the Examiner's understanding.

B. REJECTION UNDER 35 U.S.C. § 103

Claims 19-41 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over U.S. Patent Publication No. 2004/0234426 Reddy, *et al.,* ("Reddy") in view of U.S. Patent Publication No. 2016/0115017 Ostuni, *et al.,* ("Ostuni"). Applicant traverses this rejection as set forth below.

The PTO has not established a *prima facie* case of obviousness against independent claim 19 because, at a minimum, the PTO has not demonstrated that the cited references teach or suggest *each* and *every* limitation in claim 19. For example, at a minimum, the PTO has not demonstrated that the cited references teach or suggest "separation of a part of said CO2-depleted synthesis gas as fuel fraction…. wherein said separation of the fuel fraction includes the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition," as recited in independent claim 19. (emphasis added).

[1] Although the prior art status of the cited art is not being challenged at this time, Applicant reserves the right to challenge the prior art status of the cited art at any appropriate time, should the need arise. Accordingly, any arguments and amendments made herein should not be construed as acquiescing to any prior art status of the cited art.

The PTO identified the desulfurized natural gas as allegedly the sole distinguishing feature of independent claim 19 over Reddy. However, independent claim 19 also differs from Reddy at least by the fact that "said first and second streams have the same composition." This distinguishing feature is totally missing from Reddy, which on the contrary teaches to treat the CO2 depleted synthesis gas in a methanator and thereafter in a cold box or PSA in order to obtain an hydrogen rich stream and a methane rich stream. The methane rich stream is then into the burner of the primary reformer. *See, e.g., Reddy,* ¶¶[0025] and [0040]. These paragraphs from Reddy are also mentioned by the PTO on page 4, last paragraph-page 5, second paragraph of the Office Action. Thus, Reddy teaches away from the subject matter of independent claim 19.

The PTO has omitted to indicate this further substantial distinguish feature when comparing Reddy with the claimed subject matter. The PTO has also not demonstrated that such a distinguishing feature is taught or suggested by Ostuni, which does not appear relevant in this regard.

This distinguishing feature of the "first and second streams having the same composition," recited in independent claim 19, plays a substantial role in the solution of the technical problem underlying the claimed subject matter. Due to the fact that a stream of CO2-depleted synthesis gas (*i.e.,* a gas very poor in CO2 and rich in nitrogen and hydrogen) is used as a fuel in the furnace, instead of a methane rich stream as suggested by Reddy, it is advantageously possible to reduce the CO2 emissions of the process if compared to Reddy. See for instance paragraphs [0010], [0017] to [0020] of the A1 publication.

One having ordinary skill in the art aiming to solve the technical problem as set forth at paragraph [0010] of the A1 publication, by considering Reddy and Ostuni would have not been directed in an obvious manner towards the claimed process, the latter being only possible with the exercise of an inventive skill.

Therefore, the PTO has not established a *prima facie* case of obviousness against independent claim 19 based on the cited references.

Claims depending from independent claim 19 are patentable due to depending from a patentable base claim and further in view of the additional subject matter recited therein.

C. CONCLUSION

In view of the foregoing, Applicant respectfully submits that the other rejections to the claims are now moot and do not, therefore, need to be addressed individually at this time. It will be appreciated, however, that this should not be construed as Applicant acquiescing to any of the purported teachings or assertions made in the last action regarding the cited art or the pending application, including any official notice. Instead, Applicant reserves the right to challenge any of the purported teachings or assertions made in the last action at any appropriate time in the future, should the need arise. Furthermore, to the extent that the Examiner has relied on any Official Notice, explicitly or implicitly, Applicant specifically requests that the Examiner provide references supporting the teachings officially noticed, as well as provide the required motivation or suggestion to combine references with the other art of record.

For at least the foregoing reasons, Applicant respectfully submits that the pending claims are neither anticipated by nor made obvious by the applied art. In the event that the Examiner finds any remaining impediment to allowance of this application that may be clarified through a telephone interview, the Examiner is requested to contact the undersigned attorney.

The Commissioner is hereby authorized to charge payment of any of the following fees that may be applicable to this communication, or credit any overpayment, to Deposit Account No. 50-6181: (1) any filing fees required under 37 CFR § 1.16; (2) any patent application and reexamination processing fees under 37 CFR § 1.17; and/or (3) any post issuance fees under 37 CFR § 1.20. In addition, if any additional extension of time is required, which has not otherwise been requested, please consider this a petition therefor and charge any additional fees that may be required to Deposit Account No. 50-6181.

Dated this 22nd day of October, 2021.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
MARCUS S. SIMON
Registration No. 50,258
Attorney for Applicant
Dorsey & Whitney LLP
Customer No. 116407
Telephone No. 801.933.7360

MSS: hm

Electronic Patent Application Fee Transmittal	
Application Number:	16485695
Filing Date:	13-Aug-2019
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Filer:	Marcus S. Simon/Holly Morton
Attorney Docket Number:	28336WOUS01_495230-44
Filed as Small Entity	

Filing Fees for U.S. National Stage under 35 USC 371

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

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Extension - 3 months with $0 paid	2253	1	740	740
Miscellaneous:				
		Total in USD ($)		**740**

Electronic Acknowledgement Receipt	
EFS ID:	44097473
Application Number:	16485695
International Application Number:	
Confirmation Number:	3128
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Customer Number:	116407
Filer:	Marcus S. Simon/Holly Morton
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	28336WOUS01_495230-44
Receipt Date:	22-OCT-2021
Filing Date:	13-AUG-2019
Time Stamp:	11:33:55
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$740
RAM confirmation Number	E20210LB34204098
Deposit Account	506181
Authorized User	Holly Morton
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.492 (National application filing, search, and examination fees) 37 CFR 1.21 (Miscellaneous fees and charges)	

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		20211022_283386WOUS01_495230-44_Amendment_A.pdf	64801 e5f4fc5f22c5b1c83f631ec82fc2a120f4f5be9a	yes	8

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Claims	2	5
	Applicant Arguments/Remarks Made in an Amendment	6	8

Warnings:

Information:

2	Fee Worksheet (SB06)	fee-info.pdf	38528 7608542a1236f868c684d7bacd34b2fd5adefea0	no	2

Warnings:

Information:

Total Files Size (in bytes):	103329

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New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 16/485,695	Filing Date 08/13/2019	☐ To be Mailed

ENTITY: ☐ LARGE ☑ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)			
FOR	NUMBER FILED	NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $50 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $230 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	10/22/2021	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 23	Minus	** 23	= 0		x $50 =	0
	Independent (37 CFR 1.16(h))	* 2	Minus	*** 3	= 0		x $240 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	SLIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/KATARA D SINGLETARY/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

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

NOTICE OF ALLOWANCE AND FEE(S) DUE

116407 7590 11/18/2021
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER
PARSA, JAFAR F

ART UNIT	PAPER NUMBER
1622	

DATE MAILED: 11/18/2021

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/485,695	08/13/2019	Francesco Baratto	28336WOUS01_495230-44	3128

TITLE OF INVENTION: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$600	$0.00	$0.00	$600	02/18/2022

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

116407 7590 11/18/2021
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/485,695	08/13/2019	Francesco Baratto	28336WOUS01_495230-44	3128

TITLE OF INVENTION: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	SMALL	$600	$0.00	$0.00	$600	02/18/2022

EXAMINER	ART UNIT	CLASS-SUBCLASS
PARSA, JAFAR F	1622	423-352000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-09 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑Issue Fee ❑Publication Fee (if required) ❑Advance Order - # of Copies _____

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29

❑ Applicant asserting small entity status. See 37 CFR 1.27

❑ Applicant changing to regular undiscounted fee status.

NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

Topsoe, Inc. – EX1002
Page 324 of 356

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
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Alexandria, Virginia 22313-1450
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/485,695	08/13/2019	Francesco Baratto	28336WOUS01_495230-44	3128

116407 7590 11/18/2021

Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER	
PARSA, JAFAR F	
ART UNIT	**PAPER NUMBER**
1622	

DATE MAILED: 11/18/2021

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/485,695	Applicant(s) Baratto et al.	
	Examiner JAFAR F PARSA	Art Unit 1622	AIA (FITF) Status Yes

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

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the remarks filed on October 22, 2021.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

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

3. ☑ The allowed claim(s) is/are See Continuation Sheet . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

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

   Certified copies:

   a) ☑ All b) ☐ Some* c) ☐ None of the:

   1. ☑ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☐ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/JAFAR F PARSA/
Primary Examiner, Art Unit 1622

Continuation of 3. The allowed claim(s) is/are: 19-41

Notice of Pre-AIA or AIA Status

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

Applicant's arguments, see the amendments/remarks, filed on October 22, 2021, with respect to the claim rejections under 35 U.S.C. 103 as being unpatentable over Reddy et al (US 2004/0234426) in view of Ostuni et al (US 2016/0115017 A1) have been fully considered and are persuasive. The aforesaid claim rejection has been withdrawn.

The following is an examiner's statement of reasons for allowance:

This distinguishing feature of the first and second streams having the same composition, recited in independent claim 19 not being taught by Reddy. This feature plays a significant role in the solution of the technical problem underlying the claimed subject matter. Due to the fact that a stream of CO_2- depleted synthesis gas (i.e., a gas very poor in CO_2 and rich in nitrogen and hydrogen) is used as a fuel in the furnace, instead of a methane rich stream as suggested by Reddy, it is advantageously possible to reduce the CO_2 emissions of the process if compared to Reddy. One having ordinary skill in the art aiming to solve the technical problem as set forth at paragraph [0010] of the publication, by considering Reddy and Ostuni would have not been directed in an obvious manner towards the claimed process.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Any inquiry concerning this communication or earlier communications from the examiner should be directed to JAFAR F PARSA whose telephone number is (571)272-0643. The examiner can normally be reached M-F 10:00 AM-6:30PM.

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

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

Information regarding the status of published or unpublished applications may be obtained from Patent Center. Unpublished application information in Patent Center is available to registered users. To file and manage patent submissions in Patent Center, visit: https://patentcenter.uspto.gov. Visit https://www.uspto.gov/patents/apply/patent-center for more information about Patent Center and https://www.uspto.gov/patents/docx for information about filing in DOCX format. For additional questions, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/JAFAR F PARSA/
Primary Examiner, Art Unit 1622

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	Art Unit
	JAFAR F PARSA	1622

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

CLAIMS

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

CLAIM		DATE								
Final	Original	04/24/2021	11/06/2021							
1	19	✓	=							
2	20	✓	=							
3	21	✓	=							
4	22	✓	=							
5	23	✓	=							
6	24	✓	=							
7	25	✓	=							
8	26	✓	=							
9	27	✓	=							
10	28	✓	=							
11	29	✓	=							
12	30	✓	=							
13	31	✓	=							
14	32	✓	=							
15	33	✓	=							
16	34	✓	=							
17	35	✓	=							
18	36	✓	=							
19	37	✓	=							
20	38	✓	=							
21	39	✓	=							
22	40	✓	=							
23	41	✓	=							

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	Art Unit
	JAFAR F PARSA	1622

CPC - Searched*		
Symbol	**Date**	**Examiner**
C01C 1/04	11/06/2021	JP
C01B 3/025, 3/48, 2203/0244, 2203/0283, 2203/042, 2203/0445, 2203/068, 2203/0827, 2203/86	11/06/2021	JP

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

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

Search Notes		
Search Notes	**Date**	**Examiner**
WEST	04/24/2021	JP
INVENTOR NAME SEARCH (PALM)	11/06/2021	JP

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
C01C	1/04	11/06/2021	JP
C01B	3/025, 3/48, 2203/0244, 2203/0283, 2203/042, 2203/0445, 2203/068, 2203/0827, 2203/86	11/06/2021	JP

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	**Art Unit**
	JAFAR F PARSA	1622

CPC						
Symbol					**Type**	**Version**
C01C	/	1	/	04	F	2013-01-01
C01B	/	3	/	025	I	2013-01-01
C01B	/	3	/	48	I	2013-01-01
C01B	/	2203	/	0244	A	2013-01-01
C01B	/	2203	/	0283	A	2013-01-01
C01B	/	2203	/	042	A	2013-01-01
C01B	/	2203	/	0445	A	2013-01-01
C01B	/	2203	/	0475	A	2013-01-01
C01B	/	2203	/	068	A	2013-01-01
C01B	/	2203	/	1241	A	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	23	
/JAFAR F PARSA/ Primary Examiner, Art Unit 1622	06 November 2021	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	4

U.S. Patent and Trademark Office — Part of Paper No.: 20211106

Topsoe, Inc. – EX1002
Page 333 of 356

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	**Art Unit**
	JAFAR F PARSA	1622

INTERNATIONAL CLASSIFICATION				
CLAIMED				
C01C1/04	/	1	/	04
C01B3/02	/	3	/	02
C01B3/48	/	3	/	48

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	23	
/JAFAR F PARSA/ Primary Examiner, Art Unit 1622	06 November 2021	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	4

U.S. Patent and Trademark Office — Part of Paper No.: 20211106

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/485,695	Baratto et al.
	Examiner	**Art Unit**
	JAFAR F PARSA	1622

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

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	23	
/JAFAR F PARSA/ Primary Examiner, Art Unit 1622	06 November 2021	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	4

U.S. Patent and Trademark Office — Part of Paper No.: 20211106

Topsoe, Inc. – EX1002
Page 335 of 356

To: simon.marcus@dorsey.com,ip.docket.slc@dorsey.com,ip.patent.sl@dorsey.com
From: PAIR_eOfficeAction@uspto.gov
Cc: PAIR_eOfficeAction@uspto.gov
Subject: Private PAIR Correspondence Notification for Customer Number 116407

Nov 18, 2021 04:07:56 AM

Dear PAIR Customer:

Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176
UNITED STATES

The following USPTO patent application(s) associated with your Customer Number, 116407 , have new outgoing correspondence. This correspondence is now available for viewing in Private PAIR.

The official date of notification of the outgoing correspondence will be indicated on the form PTOL-90 accompanying the correspondence.

Disclaimer:
The list of documents shown below is provided as a courtesy and is not part of the official file wrapper. The content of the images shown in PAIR is the official record.

Application	Document	Mailroom Date	Attorney Docket No.
16485695	NOA	11/18/2021	28336WOUS01_495230-44

To view your correspondence online or update your email addresses, please visit us anytime at https://sportal.uspto.gov/secure/myportal/privatepair.

If you have any questions, please email the Electronic Business Center (EBC) at EBC@uspto.gov with 'e-Office Action' on the subject line or call 1-866-217-9197 during the following hours:

Monday - Friday 6:00 a.m. to 12:00 a.m.

Thank you for prompt attention to this notice,

UNITED STATES PATENT AND TRADEMARK OFFICE

PATENT APPLICATION INFORMATION RETRIEVAL SYSTEM

Document Description: Issue Fee Payment (PTO-85B)

Issue Fee Transmittal Form

Application Number	Filing Date	First Named Inventor	Atty. Docket No.	Confirmation No.
16485695	13-Aug-2019	Francesco Baratto	28336WOUS01_495230-44	3128

TITLE OF INVENTION :

PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

Entity Status	Application Type	Art Unit	Class - Subclass	EXAMINER
Small	U.S. National Stage under 35 USC 371	1622	352000	

Issue Fee Due	Publication Due	Total Fee(s) Due	Date Due	Prev. Paid Fee
$600	$0	$600	18-Feb-2022	$0

1.Change of Correspondence Address and/or Indication Of Fee Address (37 CFR 1.33 & 1.363)

Current Correspondence Address:	Current Indicated Fee Address :
116407 Dorsey & Whitney / UT GENERAL 111 South Main Street 21st Floor Salt Lake City UT 84111-2176 UNITED STATES 801-933-7360 ip.docket.slc@dorsey.com	
☐ Change of correspondence address requested, system generated AIA/122-EFS form attached	☐ Fee Address indication requested, system generated SB/47-EFS form attached

2.Entity Status

Change in Entity Status

○ Applicant certifying micro entity status; system generated Micro Entity certification form attached. See 37 CFR 1.29.
Note: Absent a valid certification of micro entity status, issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment. If this box is checked, you will be prompted to choose a micro entity status on the gross income basis (37 CFR 1.29(a)) or the institution of higher education basis (37 CFR 1.29(d)), and make the applicable certification online.

◉ Applicant asserting small entity status. See 37 CFR 1.27.
Note: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

○ Applicant changing to regular undiscounted fee status.
Note: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

3.The Following Fee(s) Are Submitted:

☒ Issue Fee	☐ I authorize USPTO to apply my previously paid issue fee to the current fees due
☐ Publication Fee	☐ The Director is hereby authorized to apply my previously paid issue fee to the current fee due and to charge deficient fees to Deposit Account Number _____
☐ Advance Order - # of copies _____	☐ If **in addition to** the payment of the issue fee amount submitted with this form, there are any discrepancies in any amount(s) due, the Director is authorized to charge any deficiency, or credit any overpayment, to Deposit Account Number _____ . The **issue fee must be submitted** with this form. **If payment of the issue fee does not accompany this form, checking this box and providing a deposit account number will NOT be effective to satisfy full payment of the fee(s) due.**

4.Firm and/or Attorney Names To Be Printed

NOTE: If no name is listed, no name will be printed
For printing on the patent front page, list to be displayed as entered

1. DORSEY & WHITNEY LLP
2.
3.

5.Assignee Name(s) and Residence Data To Be Printed

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

Name	City	State	Country	Category
Casale SA	Lugano		SWITZERLAND	corporation

6.Signature

I certify, in accordance with 37 CFR 1.4(d)(4) that I am an attorney or agent registered to practice before the Patent and Trademark Office who has filed and has been granted power of attorney in this application. I also certify that this Fee(s) Transmittal form is being transmitted to the USPTO via EFS-WEB on the date indicated below.

Signature	/Marcus S. Simon, Reg.# 50258/	**Date**	02-15-2022
Name	Marcus S. Simon	**Registration Number**	50258

Electronic Patent Application Fee Transmittal

Application Number:	16485695
Filing Date:	13-Aug-2019
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Filer:	Marcus S. Simon/Eve Stark
Attorney Docket Number:	28336WOUS01_495230-44

Filed as Small Entity

Filing Fees for U.S. National Stage under 35 USC 371

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPL ISSUE FEE	2501	1	600	600
PUBL. FEE- EARLY, VOLUNTARY, OR NORMAL	1504	1	0	0
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**600**

Electronic Acknowledgement Receipt	
EFS ID:	44998677
Application Number:	16485695
International Application Number:	
Confirmation Number:	3128
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Customer Number:	116407
Filer:	Marcus S. Simon/Eve Stark
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	28336WOUS01_495230-44
Receipt Date:	15-FEB-2022
Filing Date:	13-AUG-2019
Time Stamp:	14:14:51
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$600
RAM confirmation Number	E20222EE14462398
Deposit Account	506181
Authorized User	Eve Stark
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.17 (Patent application and reexamination processing fees) 37 CFR 1.19 (Document supply fees)	

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

37 CFR 1.492 (National application filing, search, and examination fees)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Issue Fee Payment (PTO-85B)	Web85b.pdf	62535 2ec6c267f45dd4a991d5192654f711c3cd17dc06	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	40379 f5780d2855f603edea2111c494e801fe37464c39	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	102914		

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

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

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of		)
		)
	Francesco Baratto, *et al.*	)
		)
Serial No.:	16/485,695	) Art Unit
		) 1622
Filed:	August 13, 2019	)
		)
Confirmation No.:	3128	)
		)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
		)
Examiner:	Jafar F. Parsa	)
		)
Customer No.:	116407	)

COMMENTS ON STATEMENT OF REASONS FOR ALLOWANCE

VIA eFILE ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Applicant respectfully submits that the claimed invention(s) as set forth in each of the independent claims and the dependent claims must be read as a whole, and not as a single feature or subcombination of features which represent less than the entirety of the claimed invention(s) as a whole. While a particular feature or subcombination of features referred to by the Examiner in the Statement of Reasons for Allowance may represent a basis for distinguishing the claimed invention(s) over the cited art, Applicant further submits that this may not necessarily be the *sole* ground for distinguishing the claimed invention(s) over the cited art of record. Accordingly, the Examiner's statement should, in Applicant's view, not be read as constituting or meaning that the claimed invention(s) can or should be reduced to a single "feature" of the claimed invention(s) or

to a subcombination of features that is less than the entire claimed invention(s) as a whole, nor that the single feature referenced by the Examiner or subcombination of features referenced by the Examiner in the Statement of Reasons for Allowance is the only or sole grounds for distinguishing the claimed invention(s) over the cited art of record, or that Applicant necessarily agrees with any characterization of the cited art set forth in the Statement of Reasons for Allowance.

The Examiner also sets forth an interpretation of certain claim features in the Notice of Allowance. Applicant does not necessarily agree with the Examiner's claim interpretation. Applicant reserves the right to challenge the Examiner's claim interpretation in the future.

Dated this 15th day of February, 2022.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
MARCUS S. SIMON
Registration No. 50,258
Attorney for Applicant
Dorsey & Whitney LLP
Customer No. 116407
Telephone No. 801.933.7360

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	16/485,695
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2IN~~ CO2 IN ATMOSPHERE	

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

Secrecy Order 37 CFR 5.2:

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

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Francesco		Baratto	

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

City	Como	Country of Residence [i]	IT

Mailing Address of Inventor:

Address 1	Viale Varese 83		
Address 2			
City	Como	State/Province	
Postal Code	22100	Country [i]	IT

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Raffaele		Ostuni	

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

City	Lugano	Country of Residence [i]	CH

Mailing Address of Inventor:

Address 1	Via Montarina 21		
Address 2			
City	Lugano	State/Province	
Postal Code	6900	Country [i]	CH

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

Correspondence Information:

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	16/485,695
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2IN~~ CO2 IN ATMOSPHERE	

Enter either Customer Number or complete the Correspondence Information section below. For further information see 37 CFR 1.33(a).			
☐ **An Address is being provided for the correspondence Information of this application.**			
Customer Number	116407		
Email Address	ip.docket.slc@dorsey.com	Add Email	Remove Email

Application Information:

Title of the Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2IN~~ CO2 IN ATMOSPHERE		
Attorney Docket Number	28336WOUS01_495230-44	**Small Entity Status Claimed**	☒
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	4	**Suggested Figure for Publication (if any)**	

Filing By Reference:

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

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

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

Publication Information:

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

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

Representative Information:

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

Please Select One:	◉ Customer Number	○ US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	116407		

PTO/AIA/14 (02-18)
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	16/485,695
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2IN~~ CO2 IN ATMOSPHERE	

Domestic Benefit/National Stage Information:

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

Prior Application Status	Pending	Remove	
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	a 371 of international	PCT/EP2018/052358	2018-01-31

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

Foreign Priority Information:

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

			Remove
Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
17156256.4	EP	2017-02-15	
			Remove
Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)
17195305.2	EP	2017-10-06	

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

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

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

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	16/485,695
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2~~IN CO2 IN ATMOSPHERE	

Authorization or Opt-Out of Authorization to Permit Access:

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

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

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

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

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

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

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

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	16/485,695
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2IN~~ CO2 IN ATMOSPHERE	

Applicant Information:

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

Applicant 1

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

Clear

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

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

Name of the Deceased or Legally Incapacitated Inventor:	
If the Applicant is an Organization check here.	☒
Organization Name	CASALE SA

Mailing Address Information For Applicant:

Address 1	Via Pocobelli 6		
Address 2			
City	Lugano	**State/Province**	
Country	CH	Postal Code	6900
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button.

Assignee Information including Non-Applicant Assignee Information:

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

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
	Application Number	16/485,695
Title of Invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF ~~CO2IN~~ CO2 IN ATMOSPHERE	

Assignee 1

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

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button.

Signature:

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

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is a **juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

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

Signature	/Marcus S. Simon, Reg.# 50258/			Date (YYYY-MM-DD)	2022-02-15
First Name	Marcus S.	Last Name	Simon	Registration Number	50258

Additional Signature may be generated within this form by selecting the Add button.

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	28336WOUS01_495230-44
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This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The information provided by you in this form will be subject to the following routine uses:

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

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

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

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

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

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

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

Electronic Acknowledgement Receipt	
EFS ID:	44998868
Application Number:	16485695
International Application Number:	
Confirmation Number:	3128
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	Francesco Baratto
Customer Number:	116407
Filer:	Marcus S. Simon/Eve Stark
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	283386WOUS01_495230-44
Receipt Date:	15-FEB-2022
Filing Date:	13-AUG-2019
Time Stamp:	14:17:50
Application Type:	U.S. National Stage under 35 USC 371

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Miscellaneous Incoming Letter	283386WOUS01_495230-44_CommentsReasonAllowance.pdf	316151 1f6f56a71bb5d6bb9348fccd39eec64bc2fc17ed	no	2

Warnings:

Information:					
2	Application Data Sheet	283386WOUS01_495230-44_CorrectedADS-Title.pdf	136743 8752c87ca88cb21dc3ad41b66da1b3d70a1c328e	no	8
Warnings:					
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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

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

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

New International Application Filed with the USPTO as a Receiving Office

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

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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/485,695	03/29/2022	11286168	283386WOUS01_495230-44	3128

116407 7590 03/09/2022

Dorsey & Whitney / UT GENERAL
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Salt Lake City, UT 84111-2176

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 66 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

INVENTOR(s) (Please see PAIR WEB site http://pair.uspto.gov for additional inventors):

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APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

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To: simon.marcus@dorsey.com,ip.docket.slc@dorsey.com,ip.patent.sl@dorsey.com
From: PAIR_eOfficeAction@uspto.gov
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Mar 10, 2022 04:59:09 AM

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Salt Lake City, UT 84111-2176
UNITED STATES

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Application	Document	Mailroom Date	Attorney Docket No.
16485695	ISSUE.NTF	03/09/2022	283386WOUS01_495230-44

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If you have any questions, please email the Electronic Business Center (EBC) at EBC@uspto.gov with 'e-Office Action' on the subject line or call 1-866-217-9197 during the following hours:

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