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APPLICATION #  
**17/905,448**

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ATTORNEY DOCKET #  
**2110-0010**

### Title of Invention

HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### Application Information

|                        |                                                |                      |                       |
|------------------------|------------------------------------------------|----------------------|-----------------------|
| APPLICATION TYPE       | Utility - U.S. National Stage under 35 USC 371 | PATENT #             | -                     |
| CONFIRMATION #         | 8205                                           | FILED BY             | Paul Craane           |
| PATENT CENTER #        | 72048702                                       | FILING DATE          | 09/01/2022            |
| CUSTOMER #             | 26568                                          | FIRST NAMED INVENTOR | Torkild R. Reinertsen |
| INTL. APPLICATION #    | -                                              | INTL. FILING DATE    | -                     |
| CORRESPONDENCE ADDRESS | -                                              | AUTHORIZED BY        | -                     |

### Documents

**TOTAL DOCUMENTS: 3**

| DOCUMENT                     |         | PAGES | DESCRIPTION                                                     | SIZE (KB) |
|------------------------------|---------|-------|-----------------------------------------------------------------|-----------|
| 2110-0010-amendment.pdf      |         | 14    | -                                                               | 149 KB    |
| 2110-0010-amendment-A....pdf | (1-1)   | 1     | Amendment/Request for Reconsideration-After Non-Final Rejection | 63 KB     |
| 2110-0010-amendment-CLM.pdf  | (2-9)   | 8     | Claims                                                          | 102 KB    |
| 2110-0010-amendment-REM.pdf  | (10-14) | 5     | Applicant Arguments/Remarks Made in an Amendment                | 110 KB    |

### Digest

Topsoe Inc. v. L'Air Liquide, SA  
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**DOCUMENT****MESSAGE DIGEST(SHA-512)**

|                                 |                                                                                                                                          |
|---------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| 2110-0010-amendment.pdf         | C8D939E4B3BE0614AD4698B3DBE39568689C5360F78B1E9D9<br>1E5A57397D6CDDDDF9755821ED52EB2AA9F3C5D3DACECC4<br>3ABD370EDD15D29AF42C27F9BF52CDAF |
| 2110-0010-amendment-A....pdf    | 7C79B4973E358FAEB57F105E4350D4316D59E6001E4ECBB22<br>A11943AA268485B1620CBDC4AF59C5461DDC883818235D85E<br>91175ADF016BD09135F77FC382012D |
| 2110-0010-amendment-<br>CLM.pdf | 42C08C4B059D27B75B0AA7B7E0EF8C8BB0DEA10D5FCE375<br>E444BB7B4D4E88C004563C6A200661CCC8F9265746D606FBA<br>57681154E77C97170D5FECC945C0CF13 |
| 2110-0010-amendment-<br>REM.pdf | 8E05FC011570977C27A466946A4E2CD0AC651E903A806FDDC<br>A4F66A32B7991B2439401B721B320330456515476406D5925D<br>DA679E322B65629370711B76B1430 |

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If a new application is being filed and the application includes the necessary components for 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

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. 17/905,448

Confirmation No. 8205

Inventor(s): Torkild R. Reinertsen et al.

Filed: February 23, 2021

Art Unit: 1736

Examiner: SPEER, Joshua Maxwell

Attorney's Docket No. 2110-0010

Customer No. 26568

Title: Hydrogen and/or Ammonia Production Process

MS AMENDMENT

Commissioner for Patents

P. O. Box 1450

Alexandria, VA 22313-1450

**AMENDMENT**

Sir:

In response to the Office Action of May 28, 2025, please amend the above-identified application as follows:

**Amendments to the Claims** are reflected in the listing of claims that begins on page 2 of this paper.

**Remarks/Arguments** begin on page 10 of this paper.

**Amendments to the Claims:**

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

**Listing of Claims:**

1 (currently amended). A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and

the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

wherein the portion of the rest gas that is recycled is at least 80%, ~~and more preferably at least 90%;~~

wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and



heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

Claims 2-4 (canceled).

5 (currently amended). The method according to claim 1, further comprising:

optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and

~~optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;~~

~~wherein the pre-reforming process comprises:~~

~~optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and~~

~~optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.~~

6 (currently amended). The method according to claim 1, wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

outputting hydrogen from the permeate side of the Palladium membrane; and  
outputting a hydrogen-depleted shifted gas from the retentate side of the  
Palladium membrane,

wherein the Palladium membrane is operated at a temperature between 200 and  
400 °C, ~~preferably between 250 and 350 °C, more preferably between 270 and 330 °C.~~

7 (previously presented). The method according to claim 1, wherein the  
hydrogen separation process comprises a PSA process.

Claims 8-10 (canceled).

11 (previously presented). The method according to claim 1, wherein the feed  
gas is natural gas.

12 (previously presented). The method according to claim 1, wherein the feed  
gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a  
petrochemical plant.

13 (currently amended). The method according to claim 1 wherein the reforming  
process comprises a gas-heated reforming process and the temperature of the gas  
exiting the gas-heated reforming process is in the range 400-800 °C, ~~preferably 450-700  
°C, more preferably 540-600 °C.~~

14 (previously presented). The method according to claim 1, wherein the one or more reforming processes are supplied with oxygen from an air separation unit.

15 (currently amended). The method according to claim 1, wherein the water-gas-shift process is conducted in one water-gas-shift reactor;

wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, ~~preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C;~~ and

wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

16 (previously presented). The method according to claim 1, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

17 (previously presented). The method according to claim 1, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

18 (currently amended). The method according to claim 1, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, ~~more preferably below 96%.~~

19 (previously presented). The method according to claim 1, wherein water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

20 (previously presented). The method according to claim 1, wherein water is not separated from the shifted gas before the hydrogen separation process.

Claim 21 (canceled).

22 (previously presented). The method according to claim 1, wherein the carbon dioxide separation process is conducted cryogenically.

23 (previously presented). The method according to claim 1, the method further comprising generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

24 (currently amended). A hydrogen production plant arranged to perform a method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and

recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

wherein the portion of the rest gas that is recycled is at least 80%, ~~and more preferably at least 90%;~~

wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

25 (currently amended). An ammonia production plant arranged to perform a method of producing ammonia, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas;

recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

wherein the portion of the rest gas that is recycled is at least 80%, ~~and more preferably at least 90%~~; and

generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit;

wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

26 (new). The method according to claim 1, further comprising:

performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;

wherein the pre-reforming process optionally comprises:

saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and

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adding hydrogen to the feed gas before performing the pre-reforming processes  
on the feed gas.

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## **REMARKS**

This is in response to the outstanding non-final Office Action of May 28, 2025. As the amendment is filed on August 27, 2025, the response is timely filed.

### **I. Status of the Amendments**

Prior to this response, claims 1, 2, 4-7, 11-20, and 22-25 were pending. Claims 1, 5, 6, 13, 15, 18, 24, and 25 have been amended, claims 2 and 4 have been canceled without prejudice to refile, and claim 26 has been added. Thus, claims 1, 5-7, 11-20, and 22-26 are pending.

Support for the amendments to claims 1, 24, and 25 may be found, for example, in claim 4. Support for new claim 26 may be found, for example, in claim 5.

### **II. Response to May 28 Office Action**

Claims 1, 2, 4-7, 11-20, and 22-25 are rejected under 35 U.S.C. 112 as allegedly indefinite. The applicant has amended claims 1, 6, 13, 15, 18, 24, and 25 to remove the narrow ranges. The rejections should be withdrawn.

The following claims are rejected under 35 U.S.C. 102 as allegedly anticipated by the identified references:

- claims 1, 2, 5, 7, 11, 13-15, 17, 18, 20, and 23-25 by US Pub. No. 2014/0170052 by Iaquaniello et al.;
- claim 1 by US Pub. No. 2013/0243686 to Genkin et al.;
- claims 1 and 16 by US Pub. No. 2010/0310949 to Licht et al.; and
- claims 1, 6, 19, and 22 by US Pat. No. 6090312 to Ziaka et al.



The applicant has amended independent claims 1, 24, and 25 to recite the language of claim 4. Claim 4 is not identified as anticipated by any of the cited references. Thus, claims 1, 24, and 25 and the remaining claims (that depend from claim 1) are novel.

Claim 4 is rejected under 35 U.S.C. 103 as allegedly unpatentable over Genkin et al. as evidenced by or alternatively in view of Iaquaniello. While claim 4 has been canceled, the claim language has been added to claims 1, 24, and 25 as noted above. Thus, the applicant responds to the rejection of claim 4.

Initially, the applicant disagrees with the interpretation of Genkin as it relates to the alleged correspondence of its reactors. Further, the applicant disagrees with combination of Iaquaniello with Genkin et al., particularly as Iaquaniello teaches away from the combination. Alternatively, the combination would render at least one of the references unsuitable for its intended purpose.

By way of background, the processes required to reform a feed gas, that is natural gas or another hydrocarbon containing gas, are described on at least page 8, line 15, to page 11, line 10 of the present application. The feed gas comprises a mixture of hydrocarbons with different lengths of hydrocarbon chains.

It is preferable for the reforming processes to be substantially performed on methane, and not on hydrocarbons with a longer hydrocarbon chain (such as ethane, butane, etc.). Accordingly, a **pre-reforming** process may be performed that converts the longer hydrocarbons to methane. Such a pre-reforming process is described on page 8, lines 19 to 21. The pre-reforming process is performed before the reforming processes are started.

The reforming processes have the purpose of converting the hydrocarbons in the feed gas, that pre-reforming may have converted to substantially only methane, to the desired product hydrogen as well as carbon monoxide and/or carbon dioxide. The

claimed reforming process (as recited in claim 1, for example) is first performing a gas-heated reforming process and then performing an autothermal reforming process. The efficiency of the reforming processes is high because heat from the autothermal reforming process is supplied to the gas-heated reforming process.

With regard to the disclosure in Genkin et al., a **pre-reforming** process is performed in the reactor 10, and the reactor 10 is a **pre-reforming** reactor, or “prereformer.” See para. [0073]. The purpose of the reactor 10 is clearly to convert the longer length hydrocarbons to a shorter length. See, particularly, the last two lines of paragraph [0075]. The reaction conditions (i.e. temperature, pressure and catalyst) have been set to carry out a process that converts longer hydrocarbon chains to shorter ones. As such, the reaction conditions in reactor 10 are substantially different from those in a **reforming** reactor, which has the different purpose of converting hydrocarbons to hydrogen.

In keeping with the background provided in the present application (see above) and as would be expected by one of ordinary skill in the art, the output of reactor 10 (which should be referred to as pre-reformed hydrocarbons and not reformat) is supplied to reactor 20 where a reforming process is performed. See paragraph [0080]. The reactor 10 **pre-reforms** the feed stock **before** it is **reformed** in reactor 20. Thus, there is no disclosure or teaching in Genkin et al. to use two separate **reforming** reactors.

Genkin et al.’s description of the reactor 10 occasionally refers to the reactor 10 using a **reforming** catalyst, even though the same catalyst may be referred to as a **prereforming** catalyst or a catalyst for **pre-reforming** immediately thereafter. See the first two sentences of para. [0075]. When considered in the context of Genkin et al. described above, one of ordinary skill would recognize referring to the catalyst as a reforming catalyst is a misstatement or mistake. The reactor 10 performs a **pre-reforming** process, and delivers pre-formed feed stock to be reformed in reactor 20.

Thus, the catalyst should have been referred to a **pre-reforming** catalyst throughout. Because of the similarity of the terms, it is not unexpected that such an unfortunate misstatement or mistake could occur.

Thus, reactor 10 and reactor 20 of Genkin et al. are not both reforming reactors, let alone a gas-heated reforming reactor and an autothermal reforming reactor. This is clearly the case because reactor 10 in Genkin et al. performs a pre-reforming process, not a reforming process. There is therefore nothing in Genkin et al. that renders obvious the claimed subject matter involving a heat-integrated gas-heated reforming process and autothermal reforming process, that may be performed in addition to a pre-reforming process.

With regard to Iaquaniello, the disclosure therein is only of using a catalytic partial oxidation reactor. In fact, paragraph [0017] of Iaquaniello **prejudices the skilled person against** using any other type of reactor than a catalytic partial oxidation reactor. Paragraph [0017] of Iaquaniello **specifically teaches against using steam reforming processes**. Accordingly, it would be in no way obvious for the skilled person to adapt the disclosure in Iaquaniello to use either a gas-heated reforming reactor or an autothermal reforming reactor, let alone implement both a gas-heated reforming reactor and an autothermal reforming reactor as claimed.

For the reasons provided above, the amended independent claims are both new and patentable over the cited documents.

In support of the above arguments, the applicant also presents new claim 26. Claim 26 recites performing a pre-reforming process in addition to the heat integrated gas-heated reforming process and autothermal reforming process (i.e., three separate processes are performed). It is not possible for Genkin et al. to disclose equivalent processes because Genkin et al. discloses only two processes (in reactors 10 and 20), a pre-reforming process and a reforming process. There is nothing in Genkin et al.,

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alone or in combination with Iaquaniello, that discloses or teaches a pre-reforming process and two separate reforming processes.

Reconsideration is respectfully requested. Further, if there is any matter that the Examiner would like to discuss, the Examiner is invited to contact the undersigned representative at the telephone number set forth below. In any event, the Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith to our Deposit Account No. 501039, under 2110-0010.

August 27, 2025

Respectfully submitted,  
/Paul C. Craane/  
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| APPLICATION NO.                                                           | FILING DATE | FIRST NAMED INVENTOR  | ATTORNEY DOCKET NO.   | CONFIRMATION NO. |
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| 17/905,448                                                                | 09/01/2022  | Torkild R. Reinertsen | 2110-0010             | 8205             |
| 26568                                                                     | 7590        | 05/28/2025            | EXAMINER              |                  |
| COOK ALEX LTD<br>SUITE 2004<br>200 WEST ADAMS STREET<br>CHICAGO, IL 60606 |             |                       | SPEER, JOSHUA MAXWELL |                  |
|                                                                           |             |                       | ART UNIT              | PAPER NUMBER     |
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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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## **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.

### ***Status of Application***

The preliminary amendment dated 9/1/2022 has been received and will be entered.

Claim(s) 1-2, 4-7, 11-20, and 22-25 is/are pending.

Claim(s) 1-2, 4-7, 11-20, and 22-25 is/are currently amended.

Claim(s) 3, 8-10, and 21 is/are acknowledged as cancelled.

### ***Priority***

Receipt is acknowledged of certified copies of papers required by 37 CFR 1.55.

### ***Information Disclosure Statement***

The information disclosure statement(s) (IDS) submitted on 9/1/2022 is/are in compliance with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner, except as noted below:

The four page IDS filed 9/1/2022 fails to comply with 37 CFR 1.98. Specifically, the 9/1/2022 IDS fails to provide a column that provides a space, next to each document to be considered, for the examiner's initials, and fails to identify the patent documents by inventor / applicant, patent number / patent application publication number, and issue / publication date. See 37 CFR 1.98(a)(1)(ii), 37 CFR 1.98(b)(1), and 37 CFR 1.98(b)(2). See also the two page IDS filed 9/1/2022, which complies with the rules. The four page IDS filed 9/1/2022 has been crossed off, and not considered.

***Claim Rejections - 35 USC § 112***

The following is a quotation of 35 U.S.C. 112(b):

(b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 1-2, 4-7, 11-20, and 22-25 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor (or for applications subject to pre-AIA 35 U.S.C. 112, the applicant), regards as the invention.

Claims 1, 6, 13, 15, 18, 24, and 25 all contain narrow and broad ranges in the same claim (e.g. Claim 1 recites “the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%”). When presented within the same claim preferences lead to confusion over the intended scope of the claims and are therefore indefinite, see also MPEP 2173.05(c).I. For the purpose of this Office Action the scope of the claims will be given by the broadest range claimed.

***Claim Interpretation***

Claim 1 recites “performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas”. The phrase ‘rest gas’ is not a recognized term in the art to the best of the Examiner’s knowledge. Rest gas was not fully defined in the specification however it does provide the following: “The rest gas 102 contains remnants of CO and CH<sub>4</sub> together with unseparated CO<sub>2</sub> and hydrogen.” [Page 18, Lines 11-



12]. Because rest gas is not defined as having a particular composition it is therefore the understanding of the Examiner that the phrase 'rest gas' indicates only the gas that is left over after H<sub>2</sub> and CO<sub>2</sub> separation and does not indicate a particular chemical composition is required.

***Claim Rejections - 35 USC § 102***

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(a)(1) the claimed invention was patented, described in a printed publication, or in public use, on sale, or otherwise available to the public before the effective filing date of the claimed invention.

(a)(2) the claimed invention was described in a patent issued under section 151, or in an application for patent published or deemed published under section 122(b), in which the patent or application, as the case may be, names another inventor and was effectively filed before the effective filing date of the claimed invention.

Claim(s) 1-2, 5, 7, 11, 13-15, 17-18, 20, and 23-25 is/are rejected under 35 U.S.C. 102(a)(1) as being anticipated by US 2014170052 A1 Iaquaniello et al.

Claim 1 requires "A method of producing hydrogen". Iaquaniello et al. is directed at a method of producing ammonia which requires that hydrogen first be produced from hydrocarbons. Iaquaniello et al. discloses "subjecting the hydrocarbon material to catalytic partial oxidation (CPO) so as to produce a synthesis gas comprising carbon monoxide, hydrogen and carbon dioxide" [0010].

Claim 1 further requires "the method comprising: receiving a feed gas comprising hydrocarbons". Iaquaniello et al. discloses natural gas as a hydrocarbon containing feed gas "The hydrocarbon material can be a single hydrocarbon, a mixture of hydrocarbons, or any other composition

comprising at least one hydrocarbon. Preferred sources are natural gas (CH<sub>4</sub>), liquid hydrocarbons (such as naphta), gasification of coal, biomass, and waste-to-energy gasification facilities.” [0022].

Claim 1 further requires “performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide”. Iaquaniello et al. discloses “subjecting the hydrocarbon material to catalytic partial oxidation (CPO) so as to produce a synthesis gas comprising carbon monoxide, hydrogen and carbon dioxide” [0010].

Claim 1 further requires “performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide”. Iaquaniello et al. discloses “subjecting the synthesis gas to a water gas shift reaction so as to react carbon monoxide with water under the formation of a gas mixture comprising hydrogen and carbon dioxide.” [0011].

Claim 1 further requires “performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas”. Iaquaniello et al. discloses “Preferably, herein H<sub>2</sub> is purified using a Pressure Swing Absorber after CO<sub>2</sub> removal, to yield a pure hydrogen stream and a purge gas stream” [0044]. The purge gas stream of Iaquaniello et al. is identified as a rest gas because it results from the leftovers once H<sub>2</sub> and CO<sub>2</sub> have been removed from the reformed and shifted gas.

Claim 1 further requires “and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the one or more reforming processes, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process”. Iaquaniello et al. discloses “the purge gas from PSA is recycled to the hydrotreating and then to the CPO [Catalytic Partial Oxidation] reactor.” [0044]. In this case the hydrotreating and CPO reactor are the purge gas (rest gas) being recycled to the reforming processes.

Claim 1 further requires “wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.”. Iaquaniello et al. discloses “the purge gas from PSA is recycled to the

hydrotreating and then to the CPO [Catalytic Partial Oxidation] reactor.” [0044]. Iaquaniello et al. does not explicitly state what percentage of the purge gas is recycled, however no further treatment of purge gas is disclosed and therefore it is understood that the entire purge gas stream (100%) is recycled.

Claim 2 requires “the reforming process comprises an autothermal reforming process and/or a partial oxidation reforming process.”. Iaquaniello et al. discloses “subjecting the hydrocarbon material to catalytic partial oxidation (CPO) so as to produce a synthesis gas comprising carbon monoxide, hydrogen and carbon dioxide” [0041].

Claim 5 recites “optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas”. Iaquaniello et al. discloses “As conventional, in the event that natural gas is employed, this will generally be desulphurized before being subjected to the process of the invention.” [0022].

Claim 5 further recites “and optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; wherein the pre-reforming process comprises: optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.”. Iaquaniello et al. does not disclose a pre-reforming process that includes adding water to the hydrocarbon gas, however it is noted that this is optional and therefore Iaquaniello et al. discloses all the limitations required by Claim 5. See MPEP 2143.03 for more information on optional claim limitations.

Claim 7 requires “the hydrogen separation process comprises a PSA process.”. Iaquaniello et al. discloses “Optionally, hydrogen is separated from this stream by pressure swing absorption (PSA) to yield a pure hydrogen stream and a purge gas stream” [0036].

Claim 11 requires “the feed gas is natural gas.”. Iaquaniello et al. discloses “The hydrocarbon material can be a single hydrocarbon, a mixture of hydrocarbons, or any other composition comprising at least one hydrocarbon. Preferred sources are natural gas (CH<sub>4</sub>), ...” [0022].

Claim 13 requires “the reforming process comprises a gas-heated reforming process and the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.”. Iaquaniello et al. discloses “The syngas at the outlet of the CPO reactor preferably is in the temperature range of 800° C.-1200° C.” [0061]. This overlaps with the claimed range at exactly one point, 800 °C. Iaquaniello et al. further discloses “In steam reforming, which is endothermic, usually a fuel is combusted in order to provide the energy input required for the reaction.” [0021] and given that in Fig. 1 and arrow labeled “fuel gas” is shown coming from the initial “NG feed” and to the steam reformer (SR) it is understood that the steam reformer is heated by burning natural gas.

Claim 14 requires “the one or more reforming processes are supplied with oxygen from an air separation unit.”. Iaquaniello et al. discloses oxygen from an air separation unit “Nitrogen is obtained from the Air Separation Unit (ASU) 90 where also the oxygen stream 102 is produced.” [0065] that is used in partial oxidation (reforming) “The resulting stream is mixed in a proper device, 20, with another stream containing oxygen and steam (resulting from mixing stream 102 and steam) before being fed to the CPO reactor” [0059].

Claim 15 requires “the water-gas-shift process is conducted in one water-gas-shift reactor”. Iaquaniello et al. discloses “The WGS reaction is typically carried out using either a single stage or multi stage to attain the desired degree and rate of conversion.” [0035]. It is understood that a multistage reactor is one reactor with many stages and not many reactors. Additionally, Iaquaniello et al. discloses a single stage reactor.

Claim 15 further recites “optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C”. Iaquaniello et al. discloses “the high temperature stage (HTS) operates at 300-450° C. ... The following stage can be a high, medium or low temperature stage (HTS, MTS or LTS); using MTS or LTS, the operating temperature is about 180-280° C” [0035]. Therefore Iaquaniello et al. discloses operating the water-gas-shift reactor at a temperature between 180-450 °C.

Claim 15 further recites “optionally, the water-gas-shift process comprises using a Cu-based catalyst.”. Iaquaniello et al. discloses an iron-chromium catalyst for high temperature shifts “the high temperature stage (HTS) operates at 300-450° C. and typically in the presence of an iron-based catalyst such as Fe/Cr.” [0035] and copper-zinc catalyst for low temperature shifts “The following stage can be a high, medium or low temperature stage (HTS, MTS or LTS); using MTS or LTS, the operating temperature is about 180-280° C. and typically a copper/zinc catalyst supported on alumina (Cu/Zn/Al) catalyst is used.” [0035]. Therefore Iaquaniello et al. discloses a water gas shift catalyst which comprises copper.

Claim 17 requires “no additional steam is added between the reforming processes and the water-gas-shift process.”. Iaquaniello et al. does not disclose adding additional steam prior to the water

gas shift reaction, additionally in Fig. 1 the only input to the WGS reactor is directly from the reforming process (partial oxidation in the presence of steam).

Claim 18 requires “operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.”. Iaquaniello et al. discloses “In the HTS the largest amount of CO is converted, usually more than 90% such as between 96 and 98%.” [0035]. It is noted that more conversion of CO happens in later stages, as high as 99.7-99.%, however one embodiment of the method of Iaquaniello et al. uses only a single stage and therefore would have CO conversion between 90-98% in that embodiment.

Claim 20 requires “water is not separated from the shifted gas before the hydrogen separation process.”. Iaquaniello et al. does not disclose separating water prior to the hydrogen separation process.

Claim 23 requires “generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.”. It can be seen in Fig. 1 of Iaquaniello et al. that the ammonia synthesis reactor receives hydrogen from PSA (Pressure Swing Absorption), which is a hydrogen separation process, and nitrogen from ASU (air separation unit). It is therefore understood that ammonia generation is dependent on these two streams.

Claim 24 requires “A hydrogen production plant arranged to perform a method of ...” and then lists method steps identical to Claim 1. Iaquaniello et al. discloses obtaining hydrogen (“subjecting the hydrocarbon material to catalytic partial oxidation (CPO) so as to produce a synthesis gas comprising carbon monoxide, hydrogen and carbon dioxide” [0010]) as an intermediate product and can therefore

be considered a hydrogen production plant arranged to perform the method steps of Claim 1 (see Claim 1 above).

Claim 25 requires “An ammonia production plant arranged to perform a method of ...” and then lists method steps identical to Claim 1 and 23. Iaquaniello et al. discloses producing ammonia “Disclosed is a process for the production of ammonia” [Abstract] as an intermediate product and can therefore be considered an ammonia production plant arranged to perform the method steps of Claim 1 and 23 (see Claims 1 and 23 above).

Claim(s) 1 is/are rejected under 35 U.S.C. 102(a)(1) as being anticipated by US 2013 243686 A1 Genkin et al.

Claim 1 requires “A method of producing hydrogen”. Genkin et al. discloses “A hydrogen production process” [Abstract].

Claim 1 further requires “the method comprising: receiving a feed gas comprising hydrocarbons”. Genkin et al. discloses “introducing reactants comprising steam and a hydrocarbon feed into a first reactor” [0009].

Claim 1 further requires “performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide”. Genkin et al. discloses “reacting the reactants in the presence of a reforming catalyst under reaction conditions sufficient to form a reformat comprising H<sub>2</sub>, CO, and unreacted methane and steam” [0009].

Claim 1 further requires “performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide”. Genkin et al. discloses “reacting the cooled reformat in the presence of a shift catalyst under reaction conditions sufficient to shift the

reformat to form additional H<sub>2</sub> in the reformat" [0012]. Additionally, Genkin et al. discloses that the shift is water gas shift "reformat from reactor 20 that has been cooled in heat recovery train 50 is passed to water-gas shift reactor 60 to shift the reformat and form additional H<sub>2</sub>" [0092].

Claim 1 further requires "performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas". Genkin et al. discloses "separating the water-depleted reformat into a CO<sub>2</sub> product stream and a pressure swing adsorber feed stream comprising H<sub>2</sub> and secondary gas components" [0015] and "separating the pressure swing adsorber feed stream in a plurality of at least 4 pressure swing adsorption beds, each adsorption bed containing an adsorbent selective for the secondary gas components thereby forming a H<sub>2</sub> product stream and a pressure swing adsorption tail gas stream" [0016]. The tail gas stream of Genkin et al. is identified as a rest gas because it results from the leftovers once H<sub>2</sub> and CO<sub>2</sub> have been removed from the reformed and shifted gas.

Claim 1 further requires "the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process". Genkin et al. discloses "introducing a second portion of the tail gas stream into at least one of the plurality of pressure swing adsorption beds" [0018]. It is noted that pressure swing adsorption beds are required of the hydrogen separation process.

Claim 1 further requires "wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.". Genkin et al. discloses "The process of aspect 1 or aspect 2 wherein the molar flow rate of the second portion of the tail gas stream is 5% to 80% or 40% to 55% of the molar flow rate of the tail gas stream." [0020]. This overlaps with the claimed invention at exactly one point, 80%.



Claim(s) 1 and 16 is/are rejected under 35 U.S.C. 102(a)(1) as being anticipated by US  
2010310949 A1 Licht et al.

Claim 1 requires “A method of producing hydrogen”. Licht et al. is directed to “A process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional hydrogen production processes.” [Abstract].

Claim 1 further requires “the method comprising: receiving a feed gas comprising hydrocarbons”. Licht et al. discloses “introducing a process stream comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane” [0007].

Claim 1 further requires “performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide”. Licht et al. discloses “to form a reformat stream comprising hydrogen, carbon monoxide, methane and steam” [0007].

Claim 1 further requires “performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide”. Licht et al. discloses “reacting the reformat stream in the presence of a shift catalyst” [0008].

Claim 1 further requires “performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas”. Licht et al. discloses “scrubbing the second process stream with a wash stream to form a carbon dioxide-depleted stream” [0009] and “separating the carbon dioxide-depleted stream to form the hydrogen-containing product gas and a by-product gas comprising methane and carbon monoxide” [0010]. The by-product gas is identified as a rest gas because it results from the leftovers once H<sub>2</sub> and CO<sub>2</sub> have been removed from the reformed and shifted gas.

Claim 1 further requires “and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process”. Licht et al. discloses “introducing a portion of the by-product gas into the process stream at a location upstream of the plurality of catalyst-containing reformer tubes and/or into the reformat stream at a location upstream of a reforming catalyst in a secondary reforming reactor” [0011]. The secondary reforming reactor is identified as the water gas shift process.

Claim 1 further requires “wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.”. Licht et al. discloses “50% to 98% by volume of the by-product gas formed in step (d) may be introduced into the process stream in step (e).” [0013].

Claim 16 requires “the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.”. Licht et al. does not explicitly disclose that the water gas shift process and hydrogen separation processes happen at the same temperature, however it is noted that unlike similar processes (Iaquaniello et al. and Genkin et al.) Licht et al. does not disclose any cooling of the stream between leaving the water gas shift reactor and entering the hydrogen separator, see [0043-0047]. It is understood by the Examiner that if the stream is neither heated nor cooled then it is implicitly disclosed to be at approximately the same temperature.

Claim(s) 1, 6, 19, and 22 is/are rejected under 35 U.S.C. 102(a)(1) as being anticipated by US 6090312 A Ziaka et al.

Claim 1 requires “A method of producing hydrogen”. Ziaka et al. is directed at a method of making hydrogen “pure hydrogen can be recovered and used in chemical syntheses and as fuel” [Abstract].

Claim 1 further requires “the method comprising: receiving a feed gas comprising hydrocarbons”. Ziaka et al. discloses “The invention describes processes that convert gaseous hydrocarbons and hydrocarbon mixtures via steam reforming” [Column 2, Line 66 – Column 3, Line 1].

Claim 1 further requires “performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide”. Ziaka et al. discloses “The invention describes processes that convert gaseous hydrocarbons and hydrocarbon mixtures via steam reforming, carbon dioxide reforming, combined steam-carbon dioxide reforming, also carbon monoxide via the water gas shift reaction, to hydrogen, carbon monoxide and carbon dioxide products” [Column 2, Line 66 – Column 3, Line 4].

Claim 1 further requires “performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide”. Ziaka et al. discloses “The invention describes processes that convert gaseous hydrocarbons and hydrocarbon mixtures via steam reforming, carbon dioxide reforming, combined steam-carbon dioxide reforming, also carbon monoxide via the water gas shift reaction, to hydrogen, carbon monoxide and carbon dioxide products” [Column 2, Line 66 – Column 3, Line 4].

Claim 1 further requires “performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas”. Ziaka et al. discloses “the hydrogen and carbon dioxide to be separated in downstream membrane permeators, consecutively placed after the reactors.” [Column 3, Lines 5-7] and “The exiting from the permeator reject (non-permeating) gases” [Column 3, Lines 33-34]. The permeator reject gases are identified as rest gas because it results from the leftovers once H<sub>2</sub> and CO<sub>2</sub> have been removed from

the reformed and shifted gas. Ziaka et al. further discloses separating H<sub>2</sub> from CO<sub>2</sub> to generate separate streams of H<sub>2</sub> and CO<sub>2</sub> "Alternatively, CO<sub>2</sub> can be condensed cryogenically from the binary mixture, and the final H<sub>2</sub> product can be used for chemical synthesis or as fuel" [Column 10, Lines 47-49].

Claim 1 further requires "the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process". Ziaka et al. discloses "The exiting from the permeator reject (non-permeating) gases which are mainly unreacted hydrocarbons and carbon monoxide are recycled into the inlet of the initial reactors for continuous reaction or fed into consecutively placed catalytic reactors which are conducting hydrocarbon steam reforming and water gas shift reactions" [Column 3, Lines 33-38].

Claim 1 further requires "wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.". Ziaka et al. does not explicitly disclose what portion of the permeator reject gasses are recycled. Because no further treatment of the permeator reject gasses is disclosed it is understood that at least one embodiment of the method of Ziaka et al. involves recycling 100% of the permeate reject gasses into the water gas shift reactor.

Claim 6 requires "the hydrogen separation process comprises: inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane". Ziaka et al. discloses membranes comprising palladium "Similar permselective inorganic membranes can be also made by sols of the above inorganic oxides mixed with metals such as nickel, palladium, platinum, silver, gold, rhodium, ruthenium, rhenium, chromium, cobalt, copper, zinc" [Column 4, Lines 3-7].

Claim 6 further requires "wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;". Ziaka et al. discloses "The membrane permeators

preferably consist of several thin hollow fibers or cylindrical tubes packed within a stainless steel module which have suitable inlet and outlet ports to deliver the gas permeated through the hollow fibers or tubes.” [Column 3, Lines 40-44]. It is noted that having two sides is an intrinsic property of a membrane and as understood by the Examiner the phrases “permeate side” and “retentate side” serve merely to clarify which side is being referred to and do not suggest further structural limitations.

Claim 6 further requires “outputting hydrogen from the permeate side of the Palladium membrane; and outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane”. Ziaka et al. discloses “H<sub>2</sub> and CO<sub>2</sub> are removed in permeate stream 12 through permselective action of membrane in D. Non permeating species CH<sub>4</sub> and CO exit from permeator through stream 13 which can be called a reject stream.” [Column 6, Lines 36-40]. The reject stream is associated with the retentate side and the hydrogen and CO<sub>2</sub> are associated with the permeate side.

Claim 6 further requires “wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.”. Ziaka et al. discloses “The organic polymer and organic polymer-inorganic support membrane permeators can operate usually between 35-500 DEG C ... For the inorganic membranes higher temperatures in permeators can be used which may approach the temperature of the preceded reactor, depending also on the desired thermal design of the overall system. Inorganic materials such as those described above as membranes, usually withstand on higher temperatures and pressures than their usual polymer counterparts” [Column 5, Line 53 – Column 6 Line 14]. It is therefore understood that the inorganic membranes can also be operated between 35-500 °C or perhaps slightly higher. The language “higher temperatures in permeators can be used” is interpreted as optional language and does not require that the highest temperature possible to be used is used. Ziaka et al. does not motivate high temperatures for the membrane separation process generally, they merely acknowledge a flaw in

organic membranes (poor performance at high temperature) which would not apply to the selection of a palladium membrane.

Claim 19 requires “water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.”. Ziaka et al. discloses “Non permeating CO exits from permeator through stream 10 which can be called a reject stream. Stream 10 can be recycled via valve D1 and stream 3 into the first shift reactor A for continuous shift reaction and conversion to H<sub>2</sub> and CO<sub>2</sub> products. Alternatively, by use of same valve D1, stream 10 becomes 12 which enters into E for additional shift reaction (2), and conversion to final H<sub>2</sub>, CO<sub>2</sub> products. Steam in E is provided via stream 13. Unreacted steam is removed from exit stream 14 by passing this stream through heat exchanger F.” [Column 7 Line 65 – Column 8 Line 7]. Ziaka discloses other process steps in between the gas output and the water separation, however Claim 19 does not require that the separation of water be performed immediately after the separation of H<sub>2</sub>.

Claim 22 requires “the carbon dioxide separation process is conducted cryogenically.”. Ziaka et al. discloses “Alternatively, CO<sub>2</sub> can be condensed cryogenically from the binary mixture, and the final H<sub>2</sub> product can be used for chemical synthesis or as fuel” [Column 10, Lines 47-49].

### ***Claim Rejections - 35 USC § 103***

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.

Claim(s) 12 is/are rejected under 35 U.S.C. 103 as being unpatentable over US 2014170052 A1 Iaquaniello et al.

Regarding Claim 12, Iaquaniello et al. teaches all of the limitations of Claim 1, see above. Claim 12 requires “the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.”. Iaquaniello et al. discloses “Preferred sources are natural gas (CH<sub>4</sub>), liquid hydrocarbons (such as naphta), gasification of coal, biomass, and waste-to-energy gasification facilities.” [0022]. Iaquaniello et al. does not disclose the source of the hydrocarbon feed, however it would have been obvious to source natural gas or gasified coal and/or biomass from an oil refinery or petrochemical plant because those are well known sources of the feedstock material.

Claim(s) 4 is/are rejected under 35 U.S.C. 103 as being unpatentable over US 2013 243686 A1 Genkin et al. as evidenced by, or alternatively in view of US 2014170052 A1 Iaquaniello et al.

Claim 4 requires “the reforming process comprises both a gas-heated reforming process and an autothermal reforming process”. Genkin et al. discloses “Reactor 20 is a reformer often called an “autothermal reformer” abbreviated “ATR.”” [0080] and “The reaction conditions in reactor 10 include a temperature ranging from 430° C. to 570° C.” [0076]. Therefore Genkin et al. discloses a heated reforming process and an autothermal reforming process however does not explicitly state that the heated reforming process is gas heated. It is understood by the Examiner that gas heated reforming is conventional in the art, as evidenced by Iaquaniello et al. “In steam reforming, which is endothermic, usually a fuel is combusted in order to provide the energy input required for the reaction.” [0021]. Therefore it would have been obvious for one of ordinary skill in the art to combust fuel (such as natural gas already employed in the method of Genkin et al.) to provide the energy required for the reaction.

Or alternatively, it would have been obvious for one of ordinary skill in the art to have used the gas heated CPO reactor of Iaquaniello et al. with the heat train of Genkin et al. It would have been obvious to combine the method of Iaquaniello et al. with the method of Genkin et al. because they both pertain to methods of hydrogen production comprising reforming a hydrocarbon, performing water gas shift reaction, separating  $H_2$  and  $CO_2$ , and recycling the leftover gas from separation back into the process (see Claim 1 for both methods). The motivation to use the CPO reactor of Iaquaniello et al. is that it is particularly useful when the end product is urea “it brings about an additional effect that can be put to use in accordance with the present invention. The production of urea requires the availability of carbon dioxide ( $CO_2$ ) as a reactant. Any  $CO_2$  formed in the catalytic partial oxidation, and particularly from the subsequent step of a water gas shift reaction, is present in the stream of gases that is part of a production process, and is therewith directly available as a reactant for the production of urea.” [0021]. The motivation to use the heat recovery train of Genkin et al. is that recovering waste heat requires less fuel to be burned and thus is a cost saving measure.

Claim 4 further requires “heat generated by the autothermal reforming process is supplied to the gas- heated reforming process.”. Genkin et al. discloses using the heat from an autothermal reactor to preheat the reactants going into the reformer “the step of recovering heat from the reformat from reactor 20 may comprise heating the reactants in reactor 10 by indirect heat exchange (not shown) between the reactants and the reformat from reactor 20 . Reactor 10 may be coupled (not shown) with heat recovery train 50 such that heat may be recovered from the reformat from reactor 20 and provide heat for reactor 10.” [0085].

### ***Conclusion***



Any inquiry concerning this communication or earlier communications from the examiner should be directed to JOSHUA MAXWELL SPEER whose telephone number is (703)756-5471. The examiner can normally be reached M-F 9am-5pm EST.

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, Anthony Zimmer can be reached at 571-270-3591. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

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JOSHUA MAXWELL SPEER  
Examiner  
Art Unit 1736

/J.M.S./  
Examiner, Art Unit 1736

/DANIEL C. MCCracken/  
Primary Examiner, Art Unit 1736

|                                          |                                       |  |                                                                 |             |
|------------------------------------------|---------------------------------------|--|-----------------------------------------------------------------|-------------|
| <b><i>Notice of References Cited</i></b> | Application/Control No.<br>17/905,448 |  | Applicant(s)/Patent Under<br>Reexamination<br>Reinertsen et al. |             |
|                                          | Examiner<br>JOSHUA M SPEER            |  | Art Unit<br>1736                                                | Page 1 of 1 |

**U.S. PATENT DOCUMENTS**

| * |   | Document Number<br>Country Code-Number-Kind Code | Date<br>YYYY-MM-DD | Name                  | CPC Classification | US Classification |
|---|---|--------------------------------------------------|--------------------|-----------------------|--------------------|-------------------|
| * | A | US-20140170052-A1                                | 2014-06-19         | Iaquaniello; Gaetano  | C01C1/04           | 423/359           |
| * | B | US-8715617-B2                                    | 2014-05-06         | Genkin; Eugene S.     | C01B3/48           | 423/437.1         |
| * | C | US-6090312-A                                     | 2000-07-18         | Ziaka; Zoe D.         | C01B3/501          | 44/457            |
| * | D | US-20100310949-A1                                | 2010-12-09         | Licht; William Robert | C01B3/382          | 429/420           |
|   | E |                                                  |                    |                       |                    |                   |
|   | F |                                                  |                    |                       |                    |                   |
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**FOREIGN PATENT DOCUMENTS**

| * |   | Document Number<br>Country Code-Number-Kind Code | Date<br>YYYY-MM-DD | Country | Name | CPC Classification |
|---|---|--------------------------------------------------|--------------------|---------|------|--------------------|
|   | N |                                                  |                    |         |      |                    |
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**NON-PATENT DOCUMENTS**

| * |   | Include as applicable: Author, Title, Date, Publisher, Edition or Volume, Pertinent Pages |
|---|---|-------------------------------------------------------------------------------------------|
|   | U |                                                                                           |
|   | V |                                                                                           |
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|   | X |                                                                                           |

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

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|--------------------------------------------------------------------------------------------------------------------|----------------------------------------------|---------------------------------------------------------------------|
| <b><i>Index of Claims</i></b><br> | <b>Application/Control No.</b><br>17/905,448 | <b>Applicant(s)/Patent Under Reexamination</b><br>Reinertsen et al. |
|                                                                                                                    | <b>Examiner</b><br>JOSHUA M SPEER            | <b>Art Unit</b><br>1736                                             |

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|---|-----------------|---|-------------------|---|---------------------|---|-----------------|
| ✓ | <b>Rejected</b> | - | <b>Cancelled</b>  | N | <b>Non-Elected</b>  | A | <b>Appeal</b>   |
| = | <b>Allowed</b>  | ÷ | <b>Restricted</b> | I | <b>Interference</b> | O | <b>Objected</b> |

| CLAIMS                                                                                                                                                                            |          |            |  |  |  |  |  |  |  |  |
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| <input type="checkbox"/> Claims renumbered in the same order as presented by applicant <input type="checkbox"/> CPA <input type="checkbox"/> T.D. <input type="checkbox"/> R.1.47 |          |            |  |  |  |  |  |  |  |  |
| CLAIM                                                                                                                                                                             |          | DATE       |  |  |  |  |  |  |  |  |
| Final                                                                                                                                                                             | Original | 05/22/2025 |  |  |  |  |  |  |  |  |
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|                                                                                                                                                                                   | 9        | -          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 10       | -          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 11       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 12       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 13       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 14       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 15       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 16       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 17       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 18       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 19       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 20       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 21       | -          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 22       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 23       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 24       | ✓          |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                   | 25       | ✓          |  |  |  |  |  |  |  |  |

|                                                                                                                 |                                              |                                                                     |
|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------|---------------------------------------------------------------------|
| <b><i>Search Notes</i></b><br> | <b>Application/Control No.</b><br>17/905,448 | <b>Applicant(s)/Patent Under Reexamination</b><br>Reinertsen et al. |
|                                                                                                                 | <b>Examiner</b><br>JOSHUA M SPEER            | <b>Art Unit</b><br>1736                                             |

| CPC - Searched*                                                                                                                                                                                                                                                                                                                  |            |              |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|--------------|
| Symbol                                                                                                                                                                                                                                                                                                                           | Date       | Examiner     |
| C01B3/382, C01B3/025, C01B3/48, C01B3/505, C01B2203/0233,<br>C01B2203/0244, C01B2203/0283, C01B2203/0405, C01B2203/043,<br>C01B2203/046, C01B2203/0475, C01B2203/0485, C01B2203/0495,<br>C01B2203/068, C01B2203/0844, C01B2203/1241, C01B2203/1258,<br>C01B2203/142, C01B2203/146, C01B2203/148, C01B2203/1614,<br>C01B2203/0415 | 05/22/2025 | Joshua Speer |

| 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     |
| Inventor + assignee search | 05/22/2025 | Joshua Speer |
| Keyword combination        | 05/22/2025 | Joshua Speer |
| Google Scholar search      | 05/22/2025 | Joshua Speer |

| Interference Search |                       |      |          |
|---------------------|-----------------------|------|----------|
| US Class/CPC Symbol | US Subclass/CPC Group | Date | Examiner |
|                     |                       |      |          |

|                                                   |  |
|---------------------------------------------------|--|
| /JOSHUA MAXWELL SPEER/<br>Examiner, Art Unit 1736 |  |
|---------------------------------------------------|--|

|                                                                                                                 |                                              |                                                                     |
|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------|---------------------------------------------------------------------|
| <b><i>Search Notes</i></b><br> | <b>Application/Control No.</b><br>17/905,448 | <b>Applicant(s)/Patent Under Reexamination</b><br>Reinertsen et al. |
|                                                                                                                 | <b>Examiner</b><br>JOSHUA M SPEER            | <b>Art Unit</b><br>1736                                             |

|                                                   |  |
|---------------------------------------------------|--|
| /JOSHUA MAXWELL SPEER/<br>Examiner, Art Unit 1736 |  |
|---------------------------------------------------|--|

SHEET 1 of 2

|                          |                                             |                                   |
|--------------------------|---------------------------------------------|-----------------------------------|
| Form PTO-1449 (Modified) | Atty. Docket No.<br>2110-0010               | Serial No.<br>Not Yet<br>Assigned |
|                          | Inventor(s)<br>Torkild R. Reinertsen et al. |                                   |
|                          | Filing Date<br>February 23, 2021            | Art Unit<br>Not Yet<br>Assigned   |

## U.S. PATENT DOCUMENTS

| Examiner<br>Initials | Document<br>Number | Issue or<br>Publication<br>Date | Name               | Class | Subclass | Filing Date<br>(If Appropriate) |
|----------------------|--------------------|---------------------------------|--------------------|-------|----------|---------------------------------|
|                      | 8,715,617          | 05-06-2014                      | Genkin et al.      |       |          |                                 |
|                      | 6,090,312          | 07-18-2000                      | Ziaka et al.       |       |          |                                 |
|                      | 2010/0287981       | 11-18-2010                      | Chen et al.        |       |          |                                 |
|                      | 2010/0310949       | 12-09-2010                      | Licht et al.       |       |          |                                 |
|                      | 2011/0011128       | 01-20-2011                      | Grover             |       |          |                                 |
|                      | 2012/0141368       | 06-07-2012                      | Vakil et al.       |       |          |                                 |
|                      | 2012/0291481       | 11-22-2012                      | Terrien et al.     |       |          |                                 |
|                      | 2013/0243686       | 09-19-2013                      | Genkin et al.      |       |          |                                 |
|                      | 2014/0170052       | 06-19-2014                      | Iaquaniello et al. |       |          |                                 |
|                      | 2014/0186255       | 07-03-2014                      | Jadhav             |       |          |                                 |

## FOREIGN PATENT DOCUMENTS

| Examiner<br>Initials | Document<br>Number | Publication<br>Date | Country                       | Translation |    |
|----------------------|--------------------|---------------------|-------------------------------|-------------|----|
|                      |                    |                     |                               | Yes         | No |
|                      | FR 2949772         | 03-11-2011          | France                        | See IDS     |    |
|                      | GB 2571136         | 08-21-2019          | Great Britain                 | N/A         |    |
|                      | WO91/12200         | 08-22-1991          | World Intellectual Prop. Org. | See IDS     |    |
|                      | WO2009/088971      | 07-16-2009          | World Intellectual Prop. Org. | N/A         |    |
|                      | WO2019/162236      | 08-29-2019          | World Intellectual Prop. Org. | N/A         |    |
|                      | WO2020/012018      | 01-16-2020          | World Intellectual Prop. Org. | N/A         |    |

|           |                        |                  |            |
|-----------|------------------------|------------------|------------|
| EXAMINER: | /JOSHUA MAXWELL SPEER/ | DATE CONSIDERED: | 05/22/2025 |
|-----------|------------------------|------------------|------------|

SHEET 2 of 2

|                                                                         |                                             |                                   |
|-------------------------------------------------------------------------|---------------------------------------------|-----------------------------------|
| Form PTO-1449 (Modified)<br><br><b>INFORMATION DISCLOSURE STATEMENT</b> | Atty. Docket No.<br>2110-0010               | Serial No.<br>Not Yet<br>Assigned |
|                                                                         | Inventor(s)<br>Torkild R. Reinertsen et al. |                                   |
|                                                                         | Filing Date<br>February 23, 2021            | Art Unit<br>Not Yet<br>Assigned   |

| OTHER DOCUMENTS |                                                                                                                                  |
|-----------------|----------------------------------------------------------------------------------------------------------------------------------|
|                 | Combined Search and Examination Report, counterpart App. No. GB2003317.1 (April 2, 2020) (5 pages)                               |
|                 | Combined Search and Examination Report, counterpart App. No. GB2010174.7 (August 4, 2020) (8 pages)                              |
|                 | International Search Report and Written Opinion, counterpart International App. No. PCT/EP2021/054441 (May 25, 2021) (15 pages). |
|                 | ROSTRUP-NIELSEN, <i>Production of synthesis gas</i> , Catalysis Today, Vol. 18, pp. 305-324 (1993).                              |
|                 | ROSTRUP-NIELSEN, <i>Syngas in perspective</i> , Catalysis Today, Vol. 71, pp. 243-247 (2002).                                    |
|                 |                                                                                                                                  |
|                 |                                                                                                                                  |

|                                  |                             |
|----------------------------------|-----------------------------|
| EXAMINER: /JOSHUA MAXWELL SPEER/ | DATE CONSIDERED: 05/22/2025 |
|----------------------------------|-----------------------------|

# Web Search History

| date, time           | web site       | search string                                                                 |
|----------------------|----------------|-------------------------------------------------------------------------------|
| 5/22/2025 4:45:12 PM | Google Scholar | hydrogen production from steam reforming PSA separation                       |
| 5/22/2025 4:45:19 PM | Google Scholar | hydrogen production from steam reforming PSA separation [before:2020]         |
| 5/22/2025 4:45:45 PM | Google Scholar | [before:2020] ammonia production from steam reforming PSA separation hydrogen |



## PE2E SEARCH - Search History (Prior Art)

| Ref # | Hits  | Search Query                                                                                                                                                                                                                                                                                                                                                       | DBs                                                                                                                                                                                                                                                                                | Default Operator | Plurals | British Equivalents | Time Stamp          |
|-------|-------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|---------|---------------------|---------------------|
| L1    | 1     | ((("Reinertsen") near3 ("New") near3 ("Energy") near3 ("AS"))).AS,AANM.                                                                                                                                                                                                                                                                                            | (US-PGPUB; USPAT)                                                                                                                                                                                                                                                                  | OR               | ON      | ON                  | 2025/05/19 01:20 PM |
| L2    | 115   | ((("REINERTSEN") near3 ("Torkild")) OR ((("BERNHARSEN") near3 ("Stein")) OR ((("RYTTER") near3 ("Erling")) OR ((("SCHANKE") near3 ("Dag")) OR ((("VAREIDE") near3 ("Dag")) OR ((("OSTADI") near3 ("Mohammad"))).INV.                                                                                                                                               | (US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT)                                                                                                                                                                                                                                        | OR               | ON      | ON                  | 2025/05/19 01:28 PM |
| L3    | 53145 | (C01B3/382 OR C01B3/025 OR C01B3/48 OR C01B3/505 OR C01B2203/0233 OR C01B2203/0244 OR C01B2203/0283 OR C01B2203/0405 OR C01B2203/043 OR C01B2203/046 OR C01B2203/0475 OR C01B2203/0485 OR C01B2203/0495 OR C01B2203/068 OR C01B2203/0844 OR C01B2203/1241 OR C01B2203/1258 OR C01B2203/142 OR C01B2203/146 OR C01B2203/148 OR C01B2203/1614 OR C01B2203/0415).cpc. | (US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, OA, RU, SU, WO, MC, MD, MY, NL, NO, NZ, PH, PL, PT, RO, RS, SE, SG, SI, SK, TH, TN, TR, TW, UA, VN)) | OR               | ON      | ON                  | 2025/05/19 01:31 PM |
| L4    | 91    | (L1 L2 ) AND L3                                                                                                                                                                                                                                                                                                                                                    | (US-PGPUB; USPAT; USOCR; FIT (AU, AP, AT, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, OA, RU, SU, WO, MC, MD, MY, NL, NO, NZ, PH, PL, PT, RO, RS, SE, SG, SI, SK, TH, TN, TR, TW, UA,      | OR               | ON      | ON                  | 2025/05/19 01:31 PM |

|     |           |                                                                                                                                           |                                                                                                                                                                                                                                                                             |    |    |    |                     |
|-----|-----------|-------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|----|----|---------------------|
| L5  | 10        | ("20100287981" "20100310949" "20110011128" "20120141368" "20120291481" "20130243686" "20140170052" "20140186255" "6090312" "8715617").PN. | (US-PGPUB; USPAT; USOCR)                                                                                                                                                                                                                                                    | OR | ON | ON | 2025/05/20 09:43 AM |
| L6  | 49086     | (hydrogen OR H2) near3 (separat\$4)                                                                                                       | (US-PGPUB; USPAT)                                                                                                                                                                                                                                                           | OR | ON | ON | 2025/05/22 04:38 PM |
| L7  | 19801     | (carbon ADJ dioxide OR CO2) near3 (separat\$4)                                                                                            | (US-PGPUB; USPAT)                                                                                                                                                                                                                                                           | OR | ON | ON | 2025/05/22 04:38 PM |
| L8  | 592294    | recycl\$3                                                                                                                                 | (US-PGPUB; USPAT)                                                                                                                                                                                                                                                           | OR | ON | ON | 2025/05/22 04:39 PM |
| L9  | 4730      | L6 AND L7 AND L8 AND L3                                                                                                                   | (US-PGPUB; USPAT; FIT (AU, AP, AT, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, OA, RU, SU, WO, MC, MD, MY, NL, NO, NZ, PH, PL, PT, RO, RS, SE, SG, SI, SK, TH, TN, TR, TW, UA, VN)) | OR | ON | ON | 2025/05/22 04:39 PM |
| L10 | 104854475 | (@pd OR @ptad OR @prad OR @ad OR @rlad) <"20200306"                                                                                       | (US-PGPUB; USPAT; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO)) | OR | ON | ON | 2025/05/22 04:41 PM |
| L11 | 3492      | L9 AND L10                                                                                                                                | (US-PGPUB; USPAT; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH,                          | OR | ON | ON | 2025/05/22 04:41 PM |

|     |       |                         |                                                                                                                                                                                                                                                                                                         |    |    |    |                     |
|-----|-------|-------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|----|----|---------------------|
| L12 | 53892 | palladium SAME membrane | TN, TR, TW, UA, VN, WO))<br>(US-PGPUB; USPAT; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO)) | OR | ON | ON | 2025/05/22 04:44 PM |
| L13 | 472   | L11 AND L12             | (US-PGPUB; USPAT; FIT (AP, AT, AU, BE, BG, BR, BY, CA, CH, CN, CS, CU, CZ, DD, DE, DK, EA, EE, EP, ES, FI, FR, GB, HR, HU, ID, IE, IL, IS, IT, JP, KR, LT, LU, LV, MA, MC, MD, MY, NL, NO, NZ, OA, PH, PL, PT, RO, RS, RU, SE, SG, SI, SK, SU, TH, TN, TR, TW, UA, VN, WO))                             | OR | ON | ON | 2025/05/22 04:44 PM |

## PE2E SEARCH - Search History (Interference)

There are no Interference searches to show.

PATENT  
Attorney Docket No. 2110-0010

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

|                                |   |                                    |
|--------------------------------|---|------------------------------------|
| In re application of:          | ) | Customer No.: 26568                |
|                                | ) |                                    |
| Torkild R. Reinertsen et al.   | ) | Confirmation No.: Not yet assigned |
|                                | ) |                                    |
| Serial No. Not yet assigned    | ) |                                    |
|                                | ) |                                    |
| Filed: February 23, 2021       | ) |                                    |
|                                | ) |                                    |
| Title: HYDROGEN AND/OR AMMONIA | ) |                                    |
| PRODUCTION PROCESS             | ) |                                    |
|                                | ) |                                    |
| Art Unit: Not yet assigned     | ) |                                    |
|                                | ) |                                    |
| Examiner: Not yet assigned     | ) |                                    |
|                                | ) |                                    |

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

**INFORMATION DISCLOSURE STATEMENT**

Dear Sir:

Pursuant to 37 CFR 1.56, 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the attached Form PTO-1449 (modified). It is respectfully requested that this information be expressly considered during the prosecution of this application, and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

In accordance with 37 CFR § 1.98(a)(2)(ii), Applicant has not submitted copies of the U.S. patents or publications. In accordance with 37 CFR § 1.98(a)(2), Applicant has submitted copies of the foreign patent and other (non-patent literature) documents.

Furthermore, in accordance with 37 CFR 1.98(a)(3) and MPEP 609.04(a) III., Applicant notes that French Pub. No. FR 2949772 was cited in the Combined Search and Examination Report (copy submitted herewith) by the UK Intellectual Property Office in counterpart App. No. GB 2010174.7, which search and examination report indicates the degree of relevance found by the UKIPO. Applicant also notes that PCT Pub. No. WO 91/12200 was cited in the Combined Search and Examination Report (copy submitted herewith) by the UKIPO in counterpart App. No. GB 2003317.1, which search and examination report indicates the degree of relevance found by the UKIPO. In addition, English-language machine translations of French Pub. No. FR 2949772 and PCT Pub. No. WO 91/12200 are provided herewith.

In accordance with 37 CFR 1.97(g), the filing of this Information Disclosure Statement shall not be construed to mean that a search has been made or that no other material information as defined by 37 CFR 1.56(a) exists. In accordance with 37 CFR 1.97(h), the filing of this Information Disclosure Statement shall not be construed to be an admission that any patent, publication, or other information referred to therein is "prior art" for this invention unless specifically designated as such.

Further, no inference should be drawn that any disclosure is equivalent to the subject invention. Citation of any document herein is not to be construed as an admission that any subject matter disclosed in the document is necessarily within the inventive field of endeavor, that any disclosure is necessarily prior in time to a particular date which may be relevant to the instant patent application, and/or that any disclosure is otherwise necessarily prior art with respect to the instant invention.

The right is also reserved to later set forth how the instant invention is distinguished over the disclosure of any document or other art, including the disclosure

of those documents discussed herein, that may be cited by the Examiner in rejecting a claim in the present patent application.

- ☒ 1. This Information Disclosure Statement is being filed within the following time period(s) set forth in 37 CFR § 1.97(b), and therefore no fee is believed to be due:

- ☐ Within three months of the filing date of a national application other than a continued prosecution application under § 1.53(d);
- ☒ Within three months of the date of entry of the national stage as set forth in § 1.491 in an international application;
- ☐ Before the mailing of first Office action on the merits; or
- ☐ Before the mailing of first Office action after the filing of a request for continued examination under § 1.114.

- ☐ 2. As set forth in 37 CFR § 1.97(c), this Information Disclosure Statement is being filed after the time period set forth in 37 CFR § 1.97(b) (see above) but before the mailing date of any of a final action under 37 CFR § 1.113, a notice of allowance under 37 CFR § 1.311 or an action that otherwise closes prosecution in the application. [Select either one of the statements OR the fee below, as appropriate.]

- ☐ It is hereby stated and certified with respect to this Information Disclosure Statement:

- ☐ 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; 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 § 1.56(c) more than three months prior to the filing of the Information Disclosure Statement.

- ☐ Enclosed is the fee set forth in 37 CFR § 1.17(p) or in the event no fee is enclosed, this is a request and authorization to charge the appropriate fee to Deposit Account No. 50-1039.

☐ 3. As set forth in 37 CFR § 1.97(d) this Information Disclosure Statement is being filed after the period specified in 37 CFR § 1.97(c) (see above) and on or before payment of the issue fee. It is hereby stated and certified with respect to this Information Disclosure Statement:

☐ 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; 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 § 1.56(c) more than three months prior to the filing of the Information Disclosure Statement.

Also enclosed is the fee set forth in 37 CFR § 1.17(p) or in the event no fee is enclosed, this is a request and authorization to charge the appropriate fee to Deposit Account No. 50-1039.

In summary, it is respectfully requested that this Information Disclosure Statement be considered and made of record, and that any fee required for consideration, if not authorized above, be charged to deposit account no. 50-1039.

Respectfully submitted,

Date: September 1, 2022

By: /Paul C. Craane/  
Paul C. Craane  
Registration No. 38,851  
COOK ALEX LTD.

200 West Adams Street, Suite 2004  
Chicago, IL 60606  
Phone: (312) 236-8500  
Fax: (312) 236-8176



# UNITED STATES PATENT AND TRADEMARK OFFICE

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

| APPLICATION NUMBER | FILING OR 371(C) DATE | FIRST NAMED APPLICANT | ATTY. DOCKET NO./TITLE |
|--------------------|-----------------------|-----------------------|------------------------|
| 17/905,448         | 09/01/2022            | Torkild R. Reinertsen | 2110-0010              |

**CONFIRMATION NO. 8205**

## PUBLICATION NOTICE



\*OC000000137790519\*

26568  
COOK ALEX LTD  
SUITE 2004  
200 WEST ADAMS STREET  
CHICAGO, IL 60606

**Title:**HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

**Publication No.**US-2023-0119784-A1

**Publication Date:**04/20/2023

## 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](http://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](http://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.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Management, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101



| <b>MULTIPLE DEPENDENT CLAIM<br/>FEE CALCULATION SHEET</b><br><br>Substitute for Form PTO-1360<br>(For use with Form PTO/SB/06) |          |        |                       |        |                        |        | Application Number<br><b>17905448</b>             |       | Filing Date |       |        |       |        |
|--------------------------------------------------------------------------------------------------------------------------------|----------|--------|-----------------------|--------|------------------------|--------|---------------------------------------------------|-------|-------------|-------|--------|-------|--------|
|                                                                                                                                |          |        |                       |        |                        |        | Applicant(s) <b>Torkild Reinertsen</b>            |       |             |       |        |       |        |
|                                                                                                                                |          |        |                       |        |                        |        | * May be used for additional claims or amendments |       |             |       |        |       |        |
| CLAIMS                                                                                                                         | AS FILED |        | AFTER FIRST AMENDMENT |        | AFTER SECOND AMENDMENT |        |                                                   | *     |             | *     |        | *     |        |
|                                                                                                                                | Indep    | Depend | Indep                 | Depend | Indep                  | Depend |                                                   | Indep | Depend      | Indep | Depend | Indep | Depend |
| 1                                                                                                                              | 1        |        | 1                     |        |                        |        |                                                   |       |             |       |        |       |        |
| 2                                                                                                                              |          | 1      |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 3                                                                                                                              |          | 2      | ---                   | ---    |                        |        |                                                   |       |             |       |        |       |        |
| 4                                                                                                                              |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 5                                                                                                                              |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 6                                                                                                                              |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 7                                                                                                                              |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 8                                                                                                                              |          | (1)    | ---                   | ---    |                        |        |                                                   |       |             |       |        |       |        |
| 9                                                                                                                              |          | (1)    | ---                   | ---    |                        |        |                                                   |       |             |       |        |       |        |
| 10                                                                                                                             |          | (1)    | ---                   | ---    |                        |        |                                                   |       |             |       |        |       |        |
| 11                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 12                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 13                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 14                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 15                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 16                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 17                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 18                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 19                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 20                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 21                                                                                                                             |          | (1)    | ---                   | ---    |                        |        |                                                   |       |             |       |        |       |        |
| 22                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 23                                                                                                                             |          | (1)    |                       | 1      |                        |        |                                                   |       |             |       |        |       |        |
| 24                                                                                                                             |          | (1)    | 1                     |        |                        |        |                                                   |       |             |       |        |       |        |
| 25                                                                                                                             |          | 1      | 1                     |        |                        |        |                                                   |       |             |       |        |       |        |
| 26                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 27                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 28                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 29                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 30                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 31                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 32                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 33                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 34                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 35                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 36                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 37                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 38                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 39                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 40                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 41                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 42                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 43                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 44                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 45                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 46                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 47                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 48                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 49                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| 50                                                                                                                             |          |        |                       |        |                        |        |                                                   |       |             |       |        |       |        |
| Total Indep                                                                                                                    | 1        |        | 3                     |        | 0                      |        |                                                   |       |             |       |        |       |        |
| Total Depend                                                                                                                   | 25       | ↙      | 17                    | ↙      | 0                      | ↙      |                                                   |       |             |       |        |       |        |
| Total Claims                                                                                                                   | 26       |        | 20                    |        | 0                      |        |                                                   |       |             |       |        |       |        |

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| <b>PATENT APPLICATION FEE DETERMINATION RECORD</b><br>Substitute for Form PTO-875                                                                                                                                                                                                                                                                                                                          |                                                                 |                                  |          |                                    |               | Application or Docket Number<br>17/905,448 |                    |                         |                    |                    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------|----------|------------------------------------|---------------|--------------------------------------------|--------------------|-------------------------|--------------------|--------------------|
| <b>APPLICATION AS FILED - PART I</b>                                                                                                                                                                                                                                                                                                                                                                       |                                                                 |                                  |          |                                    |               |                                            |                    |                         |                    |                    |
| (Column 1)                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                 | (Column 2)                       |          | SMALL ENTITY                       |               | OTHER THAN SMALL ENTITY                    |                    |                         |                    |                    |
| FOR                                                                                                                                                                                                                                                                                                                                                                                                        | NUMBER FILED                                                    | NUMBER EXTRA                     | RATE(\$) | FEE(\$)                            |               | RATE(\$)                                   | FEE(\$)            |                         |                    |                    |
| BASIC FEE<br>(37 CFR 1.16(a), (b), or (c))                                                                                                                                                                                                                                                                                                                                                                 | N/A                                                             | N/A                              | N/A      |                                    |               | N/A                                        | 320                |                         |                    |                    |
| SEARCH FEE<br>(37 CFR 1.16(k), (l), or (m))                                                                                                                                                                                                                                                                                                                                                                | N/A                                                             | N/A                              | N/A      |                                    |               | N/A                                        | 540                |                         |                    |                    |
| EXAMINATION FEE<br>(37 CFR 1.16(o), (p), or (q))                                                                                                                                                                                                                                                                                                                                                           | N/A                                                             | N/A                              | N/A      |                                    |               | N/A                                        | 800                |                         |                    |                    |
| TOTAL CLAIMS<br>(37 CFR 1.16(j))                                                                                                                                                                                                                                                                                                                                                                           | 20                                                              | minus 20 = *                     |          |                                    | OR            | x 100 =                                    | 0.00               |                         |                    |                    |
| INDEPENDENT CLAIMS<br>(37 CFR 1.16(h))                                                                                                                                                                                                                                                                                                                                                                     | 3                                                               | minus 3 = *                      |          |                                    |               | x 480 =                                    | 0.00               |                         |                    |                    |
| APPLICATION SIZE FEE<br>(37 CFR 1.16(s))<br>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               |                         |                    |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                 |                                  |          |                                    |               |                                            | 0.00               |                         |                    |                    |
| MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))                                                                                                                                                                                                                                                                                                                                                          |                                                                 |                                  |          |                                    |               |                                            | 0.00               |                         |                    |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                 |                                  | TOTAL    |                                    |               | TOTAL                                      | 1660               |                         |                    |                    |
| * If the difference in column 1 is less than zero, enter "0" in column 2.                                                                                                                                                                                                                                                                                                                                  |                                                                 |                                  |          |                                    |               |                                            |                    |                         |                    |                    |
| <b>APPLICATION AS AMENDED - PART II</b>                                                                                                                                                                                                                                                                                                                                                                    |                                                                 |                                  |          |                                    |               |                                            |                    |                         |                    |                    |
| (Column 1)                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                 | (Column 2)                       |          | (Column 3)                         |               | SMALL ENTITY                               |                    | OTHER THAN SMALL ENTITY |                    |                    |
| AMENDMENT A                                                                                                                                                                                                                                                                                                                                                                                                |                                                                 | CLAIMS REMAINING AFTER AMENDMENT |          | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE(\$)                                   | ADDITIONAL FEE(\$) |                         | RATE(\$)           | ADDITIONAL FEE(\$) |
|                                                                                                                                                                                                                                                                                                                                                                                                            | Total<br>(37 CFR 1.16(i))                                       | *                                | Minus    | **                                 | =             | x                                          | =                  | OR                      | x                  | =                  |
|                                                                                                                                                                                                                                                                                                                                                                                                            | Independent<br>(37 CFR 1.16(h))                                 | *                                | Minus    | ***                                | =             | x                                          | =                  | OR                      | x                  | =                  |
|                                                                                                                                                                                                                                                                                                                                                                                                            | Application Size Fee (37 CFR 1.16(s))                           |                                  |          |                                    |               |                                            |                    | OR                      |                    |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                            | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) |                                  |          |                                    |               |                                            |                    | OR                      |                    |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                 |                                  |          |                                    |               | TOTAL<br>ADD'L FEE                         |                    | OR                      | TOTAL<br>ADD'L FEE |                    |
| AMENDMENT B                                                                                                                                                                                                                                                                                                                                                                                                |                                                                 | CLAIMS REMAINING AFTER AMENDMENT |          | HIGHEST NUMBER PREVIOUSLY PAID FOR | PRESENT EXTRA | RATE(\$)                                   | ADDITIONAL FEE(\$) |                         | RATE(\$)           | ADDITIONAL FEE(\$) |
|                                                                                                                                                                                                                                                                                                                                                                                                            | Total<br>(37 CFR 1.16(i))                                       | *                                | Minus    | **                                 | =             | x                                          | =                  | OR                      | x                  | =                  |
|                                                                                                                                                                                                                                                                                                                                                                                                            | Independent<br>(37 CFR 1.16(h))                                 | *                                | Minus    | ***                                | =             | x                                          | =                  | OR                      | x                  | =                  |
|                                                                                                                                                                                                                                                                                                                                                                                                            | Application Size Fee (37 CFR 1.16(s))                           |                                  |          |                                    |               |                                            |                    | OR                      |                    |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                            | FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j)) |                                  |          |                                    |               |                                            |                    | OR                      |                    |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                 |                                  |          |                                    |               | TOTAL<br>ADD'L FEE                         |                    | OR                      | TOTAL<br>ADD'L FEE |                    |
| * If the entry in column 1 is less than the entry in column 2, write "0" in column 3.<br>** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".<br>*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".<br>The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1. |                                                                 |                                  |          |                                    |               |                                            |                    |                         |                    |                    |



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Alexandria, Virginia 22313-1450  
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|----------------------|-----------------------|------------------|
| U.S. APPLICATION NO. | FIRST NAMED INVENTOR  | ATTY. DOCKET NO. |
| 17/905,448           | Torkild R. Reinertsen | 2110-0010        |

26568  
COOK ALEX LTD  
SUITE 2004  
200 WEST ADAMS STREET  
CHICAGO, IL 60606

|                               |               |
|-------------------------------|---------------|
| INTERNATIONAL APPLICATION NO. |               |
| PCT/EP2021/054441             |               |
| I.A. FILING DATE              | PRIORITY DATE |
| 02/23/2021                    | 03/06/2020    |

**CONFIRMATION NO. 8205**  
**371 ACCEPTANCE LETTER**



\*OC00000013/179/64\*

Date Mailed: 01/12/2023

## 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)

09/01/2022

DATE OF RECEIPT OF 35 U.S.C.  
371(c)(1) and (c)(2) REQUIREMENTS

The following items have been received:

- Copy of the International Application filed on 09/01/2022
- Copy of the International Search Report filed on 09/01/2022
- Preliminary Amendments filed on 09/01/2022
- Information Disclosure Statements filed on 09/01/2022
- Inventor's Oath or Declaration filed on 09/01/2022
- Request for Immediate Examination filed on 09/01/2022
- U.S. Basic National Fees filed on 09/01/2022
- Authorize Access to Search Results filed on 09/01/2022
- Priority Documents filed on 09/01/2022
- Power of Attorney filed on 09/01/2022
- Authorization to Permit Access filed on 09/01/2022
- Application Data Sheet (37 CFR 1.76) filed on 09/01/2022

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)

BARBARA A CAMPBELL

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# UNITED STATES PATENT AND TRADEMARK OFFICE

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

| APPLICATION<br>NUMBER | FILING or<br>371(c) DATE | GRP ART<br>UNIT | FIL FEE REC'D | ATTY. DOCKET NO | TOT CLAIMS | IND CLAIMS |
|-----------------------|--------------------------|-----------------|---------------|-----------------|------------|------------|
| 17/905,448            | 09/01/2022               |                 | 1660          | 2110-0010       | 20         | 3          |

**CONFIRMATION NO. 8205**

## FILING RECEIPT

26568  
COOK ALEX LTD  
SUITE 2004  
200 WEST ADAMS STREET  
CHICAGO, IL 60606



0000000137179763

Date Mailed: 01/12/2023

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)

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Stein Bernhardsen, Heimdal, NORWAY;  
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### Applicant(s)

Reinertsen New Energy AS, Trondheim, NORWAY;

**Power of Attorney:** The patent practitioners associated with Customer Number 26568

### Domestic Priority data as claimed by applicant

This application is a 371 of PCT/EP2021/054441 02/23/2021

**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.)

UNITED KINGDOM 2003317.1 03/06/2020

UNITED KINGDOM 2010174.7 07/02/2020

**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:** 01/10/2023

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 17/905,448**

**Projected Publication Date:** 04/20/2023

**Non-Publication Request:** No

**Early Publication Request:** No

**Title**

HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

**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**

**GRANTED**

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**NOT GRANTED**

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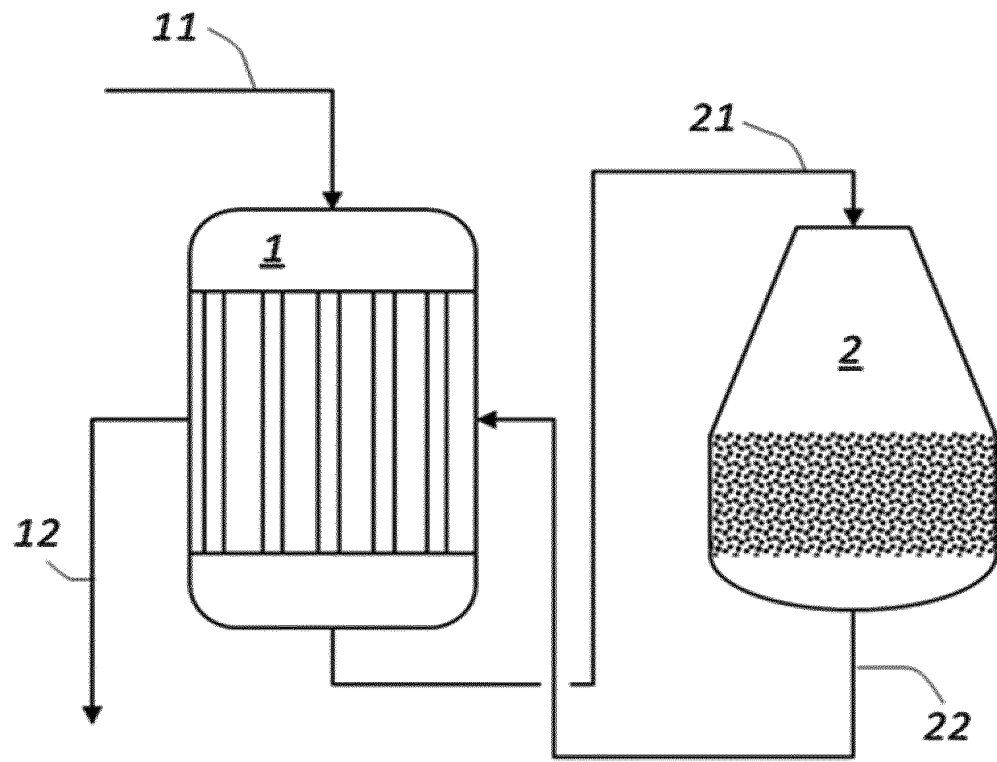


FIGURE 1



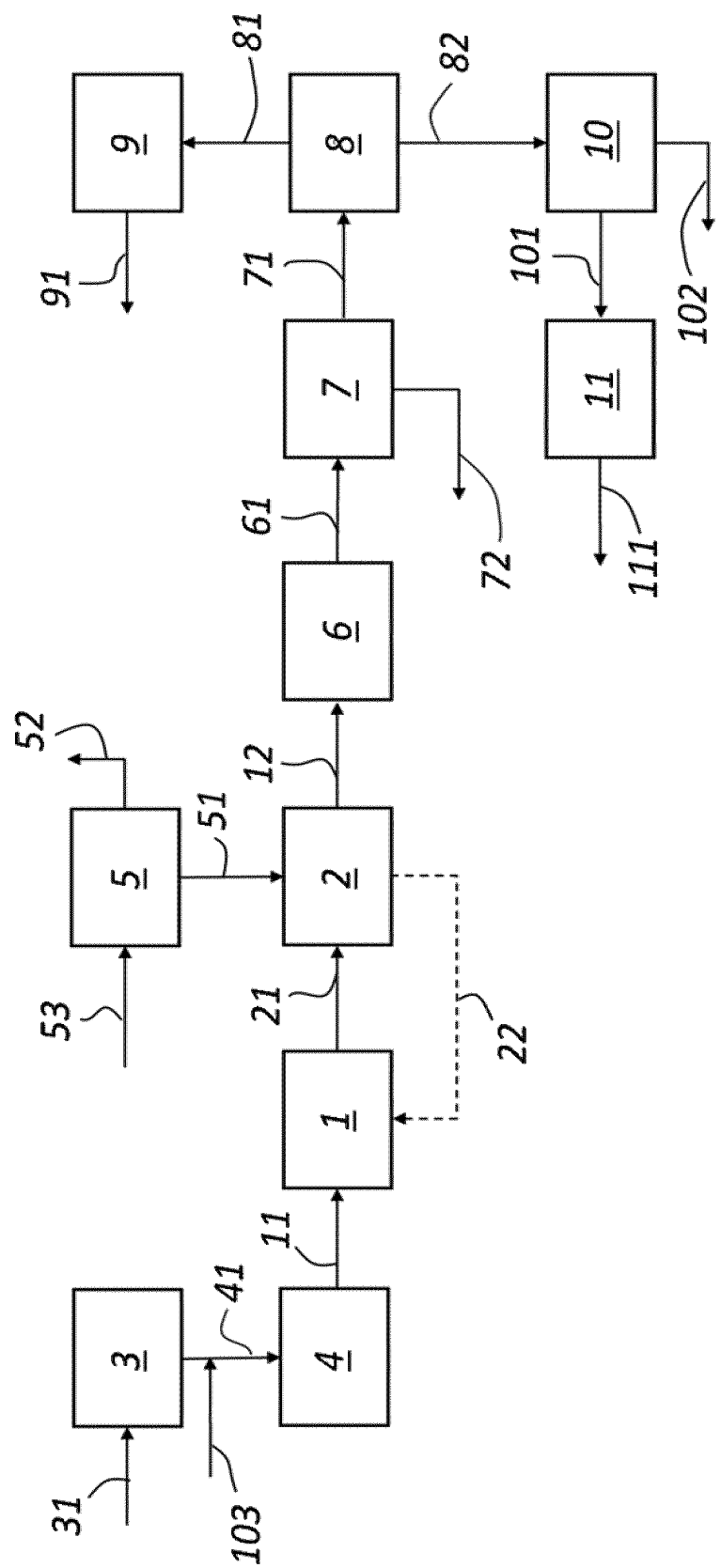


FIGURE 2

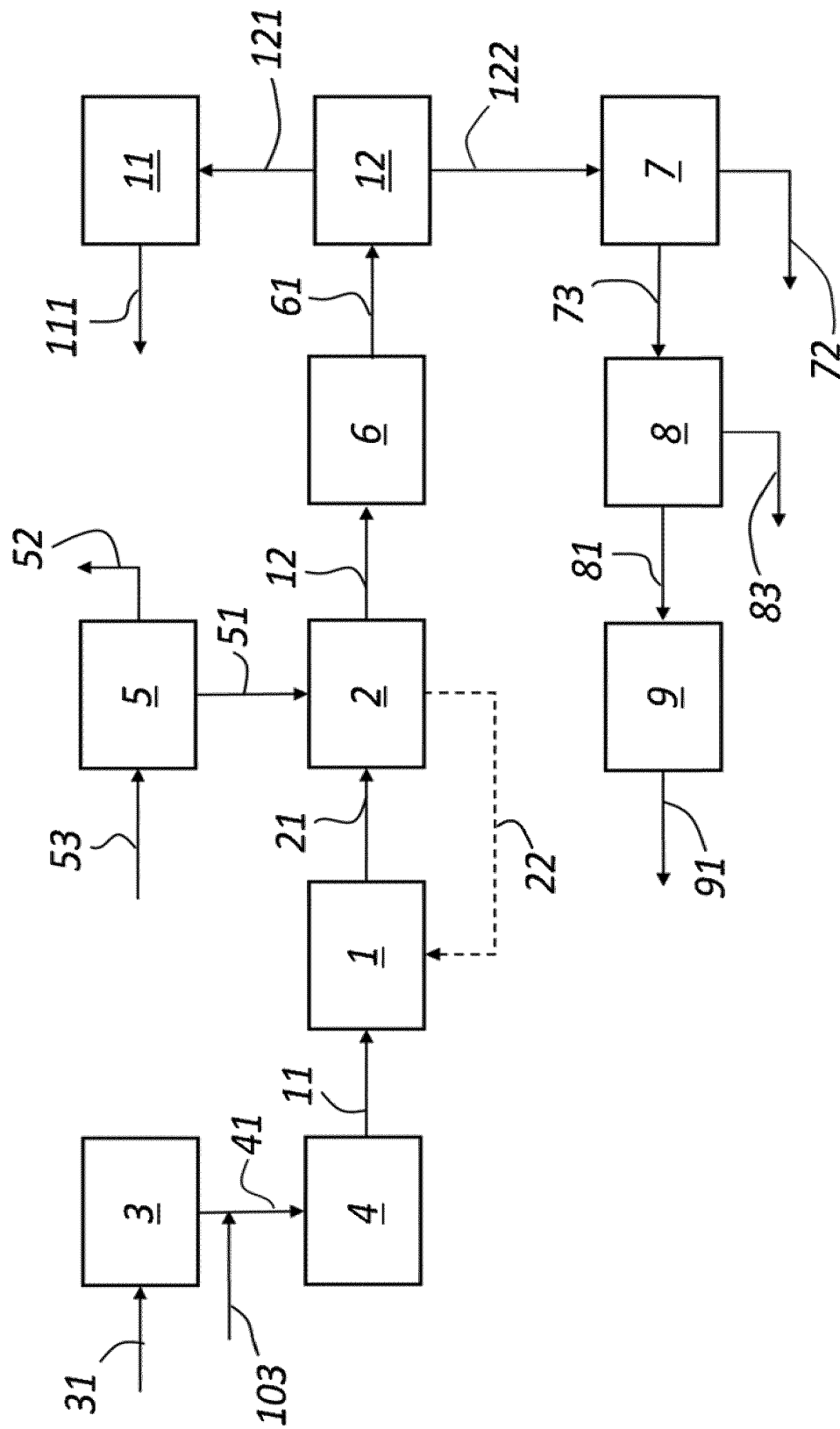


FIGURE 3

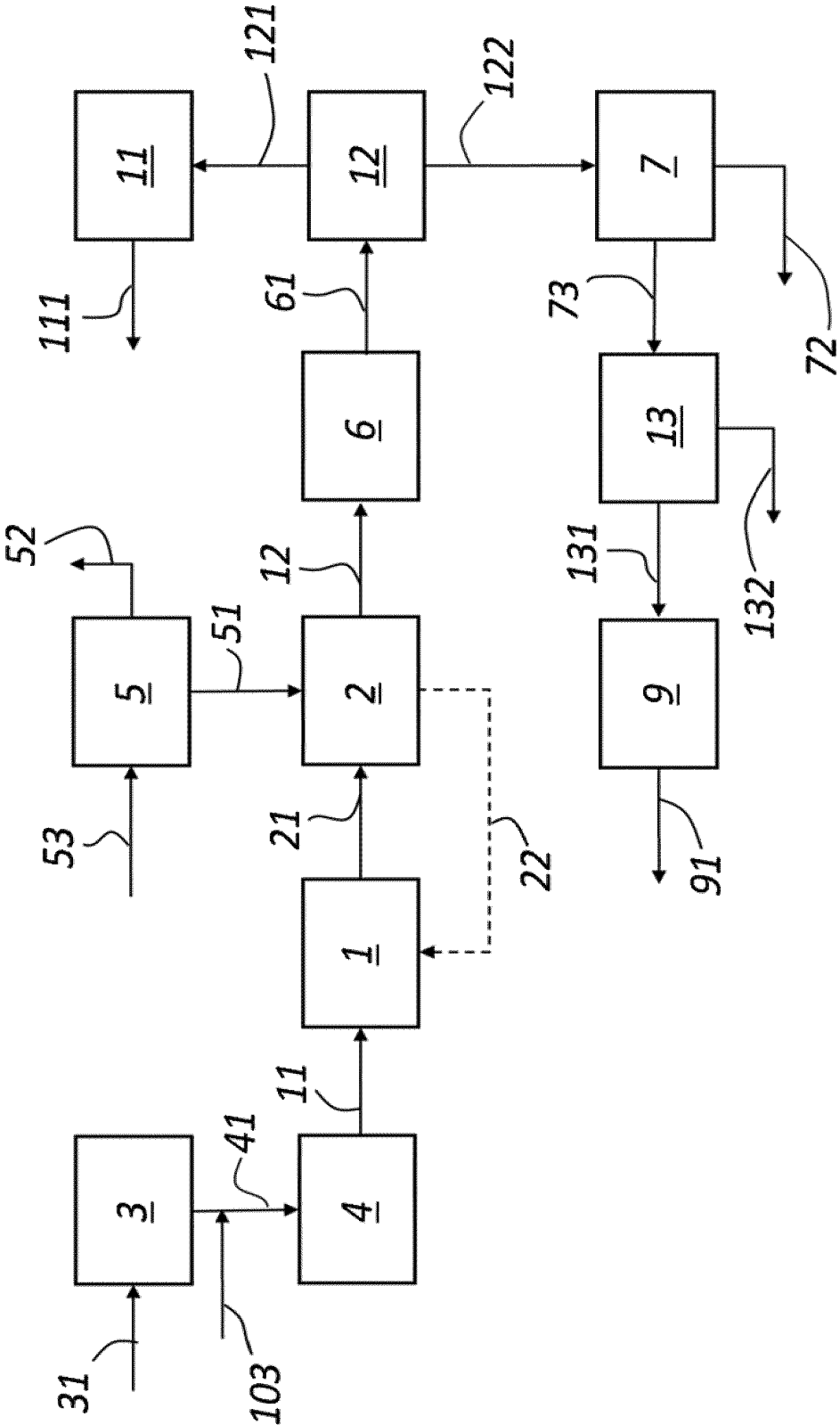


FIGURE 4

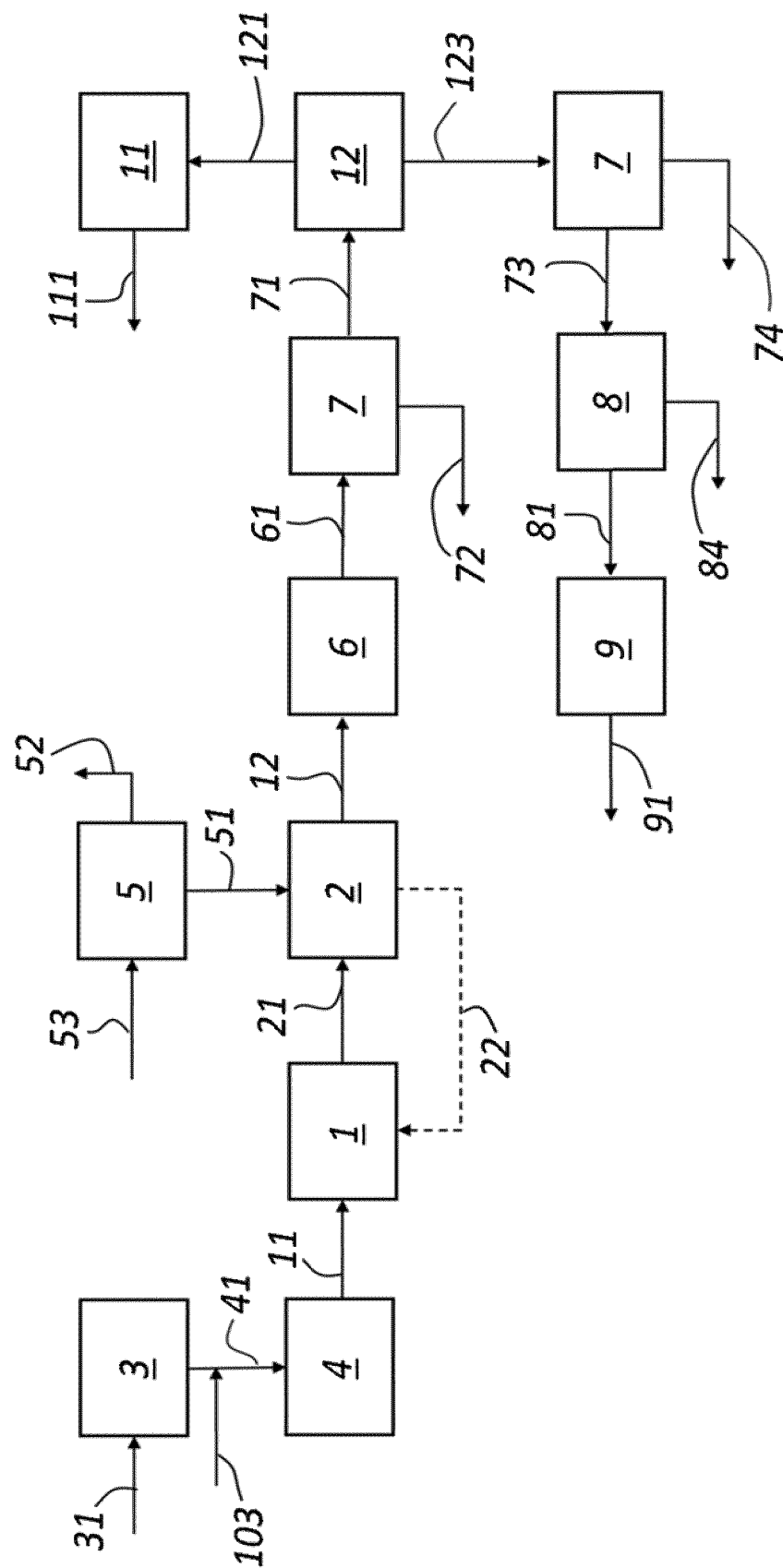


FIGURE 5

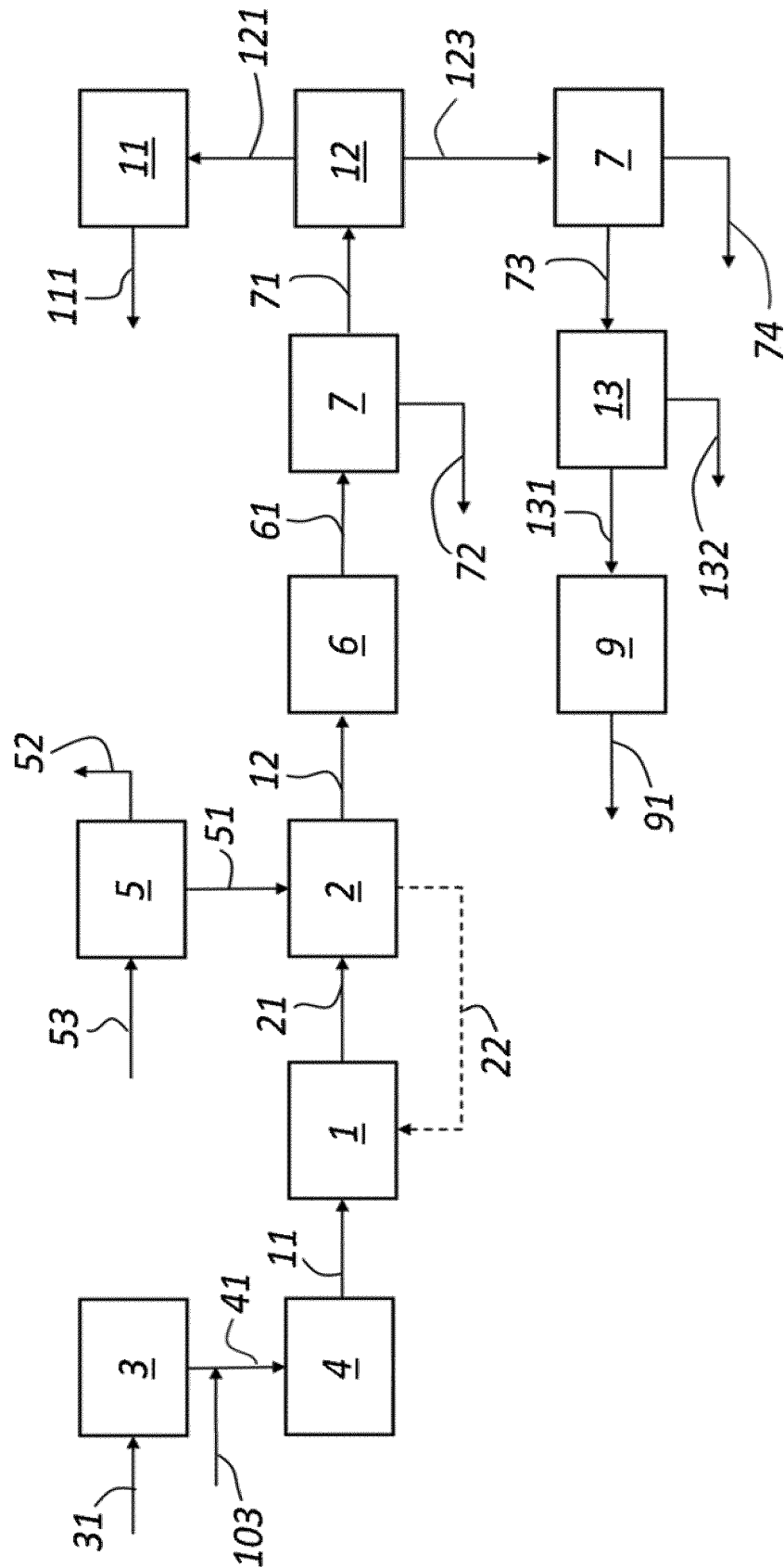


FIGURE 6

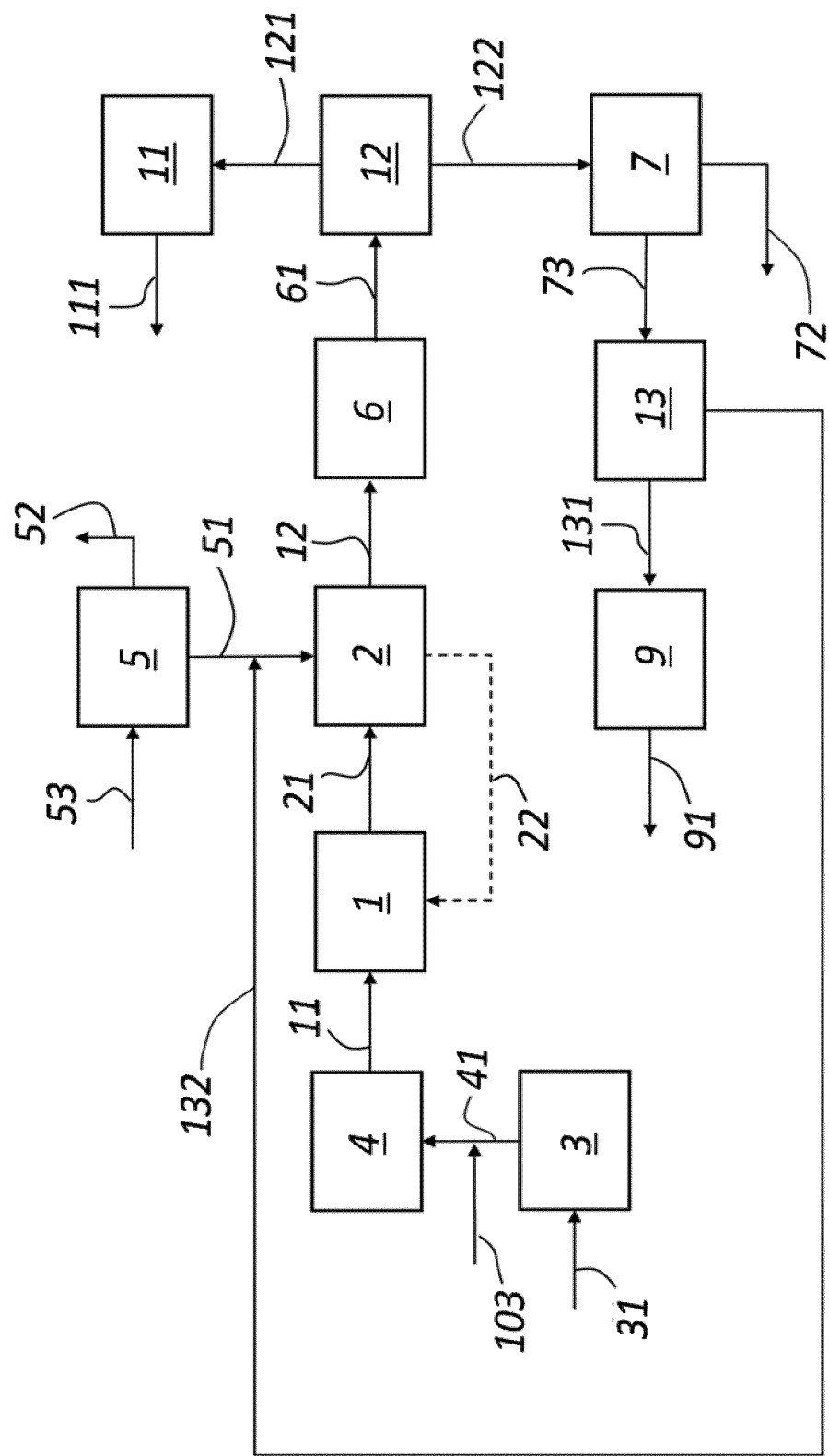


FIGURE 7

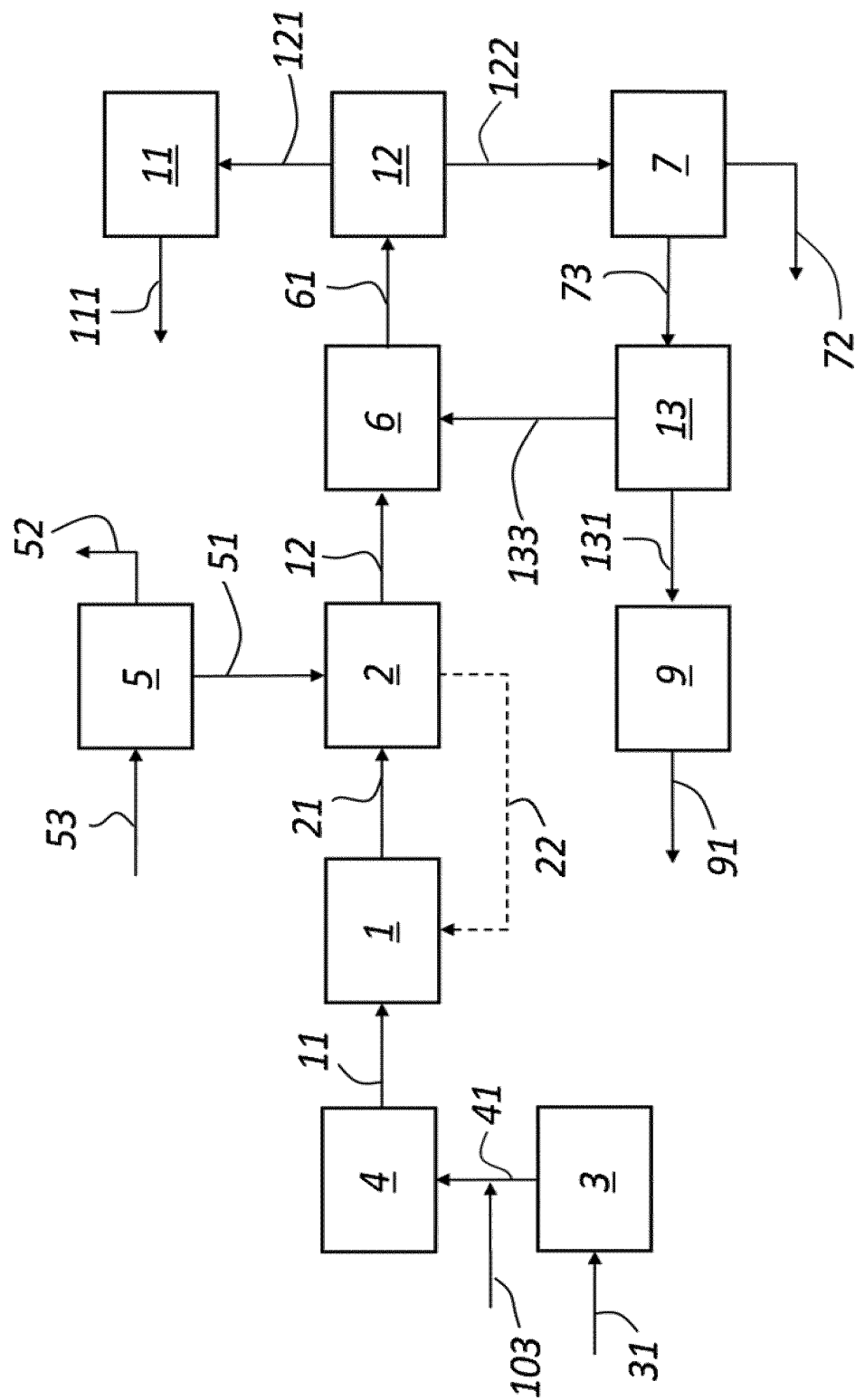


FIGURE 8

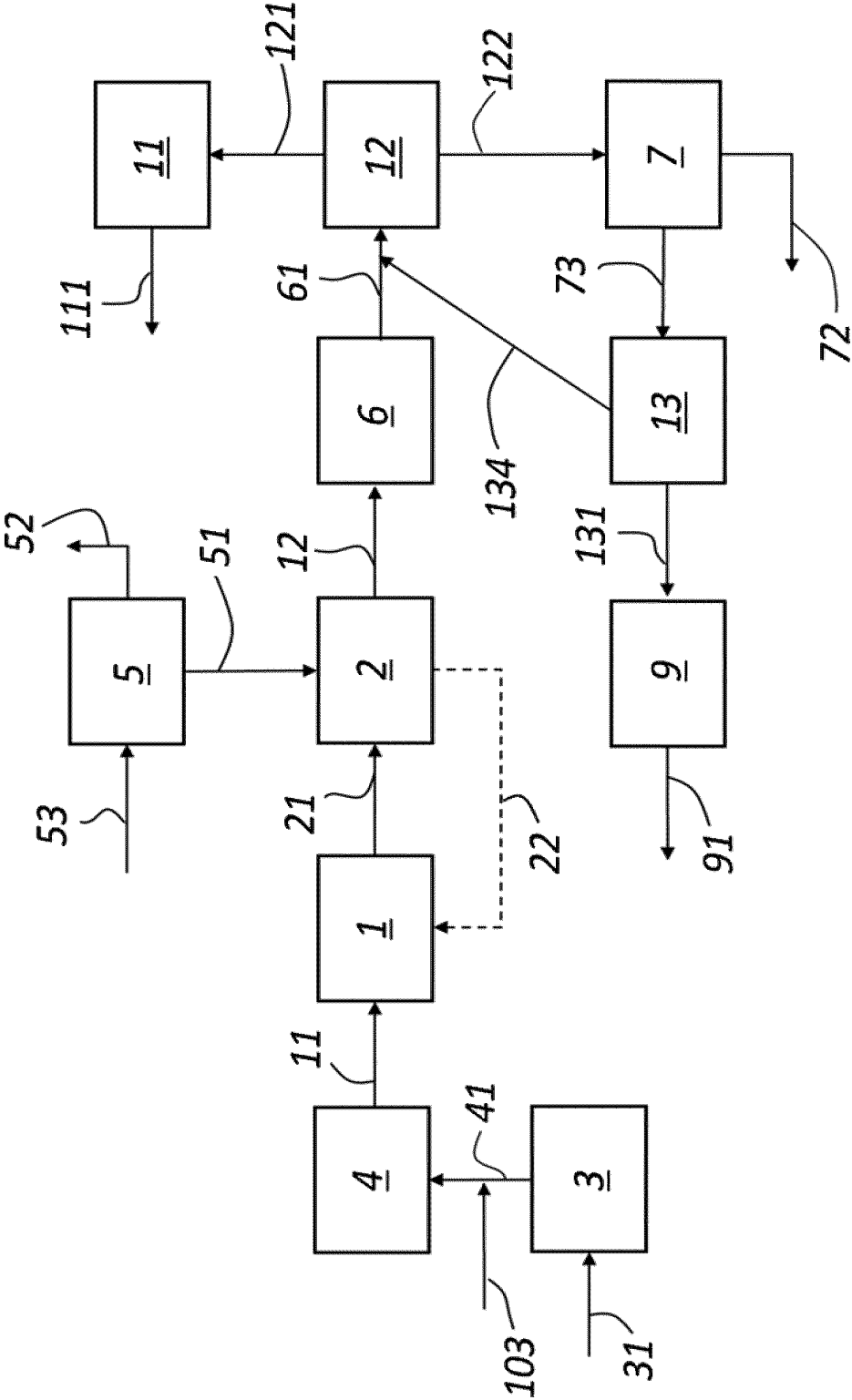


FIGURE 9



Table 1. Summary of process schemes.

|                                          | Comparative<br>Example | Embodiment<br>Example 1 | Embodiment<br>Example 2 | Embodiment<br>Example 3 | Embodiment<br>Example 4 | Embodiment<br>Examples 5-<br>7 |
|------------------------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------|
| WGS temperature<br>(°C)                  | 256                    | 300                     | 300                     | 256                     | 256                     | 300                            |
| Pd membrane                              |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Water condensation<br>directly after WGS | ✓                      |                         |                         | ✓                       | ✓                       |                                |
| Water condensation<br>after membrane     |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Amine separation                         | ✓                      | ✓                       |                         | ✓                       |                         |                                |
| Cryogenic<br>separation                  |                        |                         | ✓                       |                         | ✓                       | ✓                              |
| PSA                                      | ✓                      |                         |                         |                         |                         |                                |
| Recycle of rest-gas                      |                        |                         |                         |                         |                         | ✓                              |

FIGURE 10

Table 2.

|                                        | Comparative Example | Embodiment Example 1 | Embodiment Example 2 | Embodiment Example 3  | Embodiment Example 4 |
|----------------------------------------|---------------------|----------------------|----------------------|-----------------------|----------------------|
| Type                                   |                     | Membrane after WGS   |                      | Membrane after heater |                      |
|                                        | Base case           | Pd + Amine           | Pd + Cryo            | Pd + Amine            | Pd + Cryo            |
| H <sub>2</sub> production (kg/h)       | 1412                | 1516                 | 1516                 | 1524                  | 1524                 |
| H <sub>2</sub> production (kmol/h)     | 701                 | 752                  | 752                  | 756                   | 756                  |
| H <sub>2</sub> recovery factor (%)     | 86                  | 93                   | 93                   | 93                    | 93                   |
| Carbon capture (%) <sup>*</sup>        | 97.5                | 96                   | 90                   | 96                    | 90                   |
| CO <sub>2</sub> before capture (mol%)  | 25                  | 79                   | 79                   | 80                    | 80                   |
| Purity of CO <sub>2</sub> captured (%) | 100                 | 100                  | 99.9                 | 100                   | 99.9                 |
| CO conversion in WGS                   | 97.4                | 95.0                 | 95.0                 | 97.4                  | 97.4                 |

<sup>\*</sup> Defined as carbon captured relative to carbon in feed

FIGURE 11

Table 3. Advantages of the different examples.

| Type                                    | Comparative Example | Embodiment Example 1 | Embodiment Example 2  | Embodiment Example 3  | Embodiment Example 4  |
|-----------------------------------------|---------------------|----------------------|-----------------------|-----------------------|-----------------------|
|                                         |                     | Membrane after WGS   | Membrane after heater | Membrane after heater | Membrane after heater |
|                                         | Base case           | Pd + Amine           | Pd + Cryo             | Pd + Amine            | Pd + Cryo             |
| Cost of H <sub>2</sub> separation       |                     | +++                  | +++                   | +++                   | +++                   |
| Footprint of H <sub>2</sub> separation  |                     | ++                   | ++                    | ++                    | ++                    |
| Efficiency of H <sub>2</sub> separation |                     | +++                  | +++                   | +++                   | +++                   |
| Cost of CO <sub>2</sub> separation      |                     | +                    | ++                    | +                     | ++                    |
| Footprint of CO <sub>2</sub> separation |                     | +                    | ++                    | +                     | ++                    |
| Efficiency of CO <sub>2</sub> capture   | ++                  | +                    |                       | +                     |                       |
| Water condensation                      | ++                  | ++                   | ++                    |                       |                       |
| Heat exchange                           | ++                  | +                    | +                     |                       |                       |
| Total                                   | 6+                  | 14+                  | 15+                   | 11+                   | 12+                   |

FIGURE 12

Table 4. Effect of recycling rest-gas to ATR.

|                                     | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Recycle option                      | No recycle              | 50%                     | 80%                     | 90%                     |
| O <sub>2</sub> to ATR (kg/h)        | 4179                    | 4316                    | 4426                    | 4482                    |
| H <sub>2</sub> production (kmol/h)  | 752                     | 777                     | 794                     | 799*                    |
| Carbon capture (%)                  | 89.7                    | 94.4                    | 97.7                    | 98.8                    |
| Heat available in Fired heater (MW) | 4.6                     | 2.5                     | 1.0                     | 0.5                     |

\* Represents 99% hydrogen recovery compared to Table 2.

FIGURE 13

Table 5. Advantages of Embodiment Examples 5-7.

|                                         | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|                                         | No recycle              | 50 %                    | 80 %                    | 90 %                    |
| Cost of H <sub>2</sub> separation       | +++                     | +++                     | +++                     | +++                     |
| Footprint of H <sub>2</sub> separation  | ++                      | ++                      | ++                      | ++                      |
| Efficiency of H <sub>2</sub> separation | +++                     | +++                     | ++++                    | ++++                    |
| Cost of CO <sub>2</sub> separation      | ++                      | ++                      | ++                      | ++                      |
| Footprint of CO <sub>2</sub> separation | ++                      | ++                      | ++                      | ++                      |
| Efficiency of CO <sub>2</sub> capture   |                         | +                       | ++                      | +++                     |
| Water condensation                      | ++                      | ++                      | ++                      | ++                      |
| Heat exchange                           | +                       | +                       | +                       | +                       |
| Energy efficiency                       | ++                      | +                       |                         |                         |
| Total                                   | 17+                     | 17+                     | 18+                     | 19+                     |

FIGURE 14

Table 6. Effect of recycling 80% rest-gas compared to no recycle.

|                                        | Embodiment<br>Example 2 | Embodiment<br>Example 6 | Embodiment<br>Example 8 | Embodiment<br>Example 9 | Embodiment<br>Example 10 |
|----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| Recycle option                         | No recycle              | To ATR                  | To WGS                  | To<br>membrane          | To ATR                   |
| Recycle ratio                          | 0%                      | 80%                     | 80%                     | 80%                     | 80%                      |
| O <sub>2</sub> to ATR (kg/h)           | 4179                    | 4426                    | 4179                    | 4179                    | 4179                     |
| ATR exit (°C)                          | 1020                    | 1020                    | 1020                    | 1020                    | 989                      |
| H <sub>2</sub> production (kmol/h)     | 752                     | 798                     | 803                     | 797                     | 807                      |
| Carbon capture (%)                     | 89.7                    | 97.7                    | 97,3                    | 95,1                    | 97,5                     |
| Heat available in Fired<br>heater (MW) | 4.6                     | 1.0                     | 1,5                     | 1,9                     | 1.2                      |

FIGURE 15

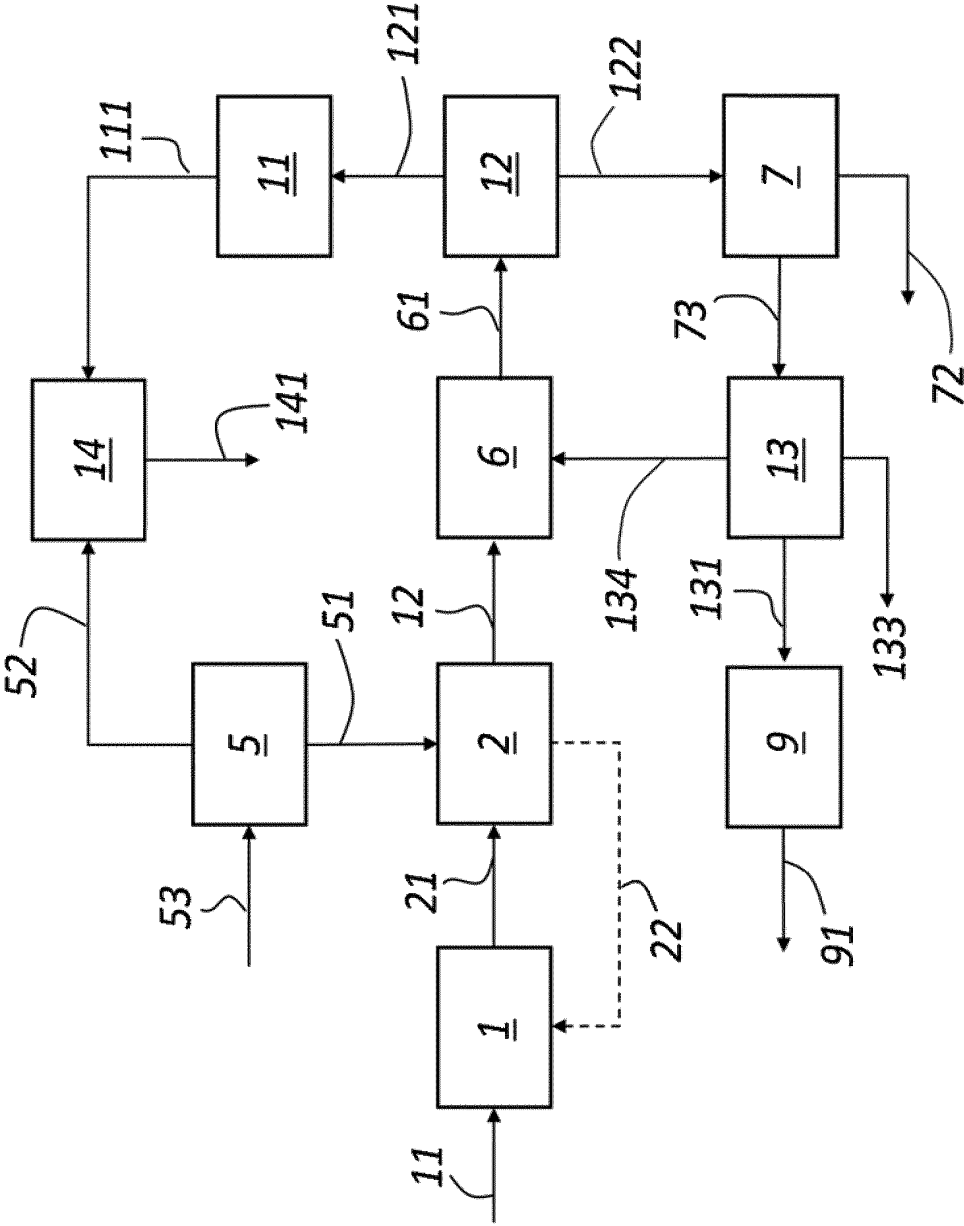


FIGURE 16

**Claims:**

1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

5 performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

10

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and

15 the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the one or more reforming processes, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

20 wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.

2. The method according to claim 1, wherein the reforming process comprises an autothermal reforming process and/or a partial oxidation reforming process

25

3. The method according to claim 1 or 2, wherein the reforming process comprises a gas heated reforming process.



4. The method according to any preceding claim, wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and

5 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

5. The method according to any preceding claim, further comprising:

10 optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and

optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;

15 wherein the pre-reforming process comprises:

optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and

20 optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

- 25 6. The method according to any preceding claim, wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

30 outputting hydrogen from the permeate side of the Palladium membrane; and

outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

- 5
7. The method according to any preceding claim, wherein the hydrogen separation process comprises a PSA process.
8. The method according to claims 2 or 4, or any claim dependent thereon, wherein the rest gas that is recycled is fed back into at least one of the one or more reforming process, and optionally the rest gas is recycled back into the autothermal reforming process.
- 10
9. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the water-gas-shift process.
10. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
- 15
11. The method according to any of the preceding claims, wherein the feed gas is natural gas.
12. The method according to any of the preceding claims, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
13. The method according to claim 3, or any claim dependent thereon, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.
- 25
14. The method according to any preceding claim, wherein the one or more reforming processes are supplied with oxygen from an air separation unit.
- 30
15. The method according to any preceding claim, wherein the water-gas-shift process is conducted in one water-gas-shift reactor;

wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C; and

5

wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

10

16. The method according to any preceding claim, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

15

17. The method according to any preceding claim, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

18. The method according to any preceding claim, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

20

19. The method according to any preceding claim, wherein water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

25

20. The method according to any preceding claim, wherein water is not separated from the shifted gas before the hydrogen separation process.

30

21. The method according to claim 6, or any claim dependent thereon, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

22. The method according to any of the preceding claims, wherein the carbon dioxide separation process is conducted cryogenically.

23. The method according to any preceding claim, the method further comprising generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

5 24. A hydrogen production plant arranged to perform the method of any of claims 1 to 22.

25. An ammonia production plant arranged to perform the method of claim 23.

10

## HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### FIELD

The present disclosure relates to hydrogen and ammonia production processes. Embodiments provide a system for generating syngas and then separating hydrogen  
5 from the syngas. The system according to embodiments may use the separated hydrogen to generate ammonia.

### BACKGROUND

It is generally believed that the greenhouse effect and the climate on Earth are  
10 closely linked to human-made emissions of carbon dioxide (CO<sub>2</sub>). These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines. A desirable goal is to reduce the emission of CO<sub>2</sub> to the atmosphere. It is known art to reduce the emission of CO<sub>2</sub> from combustion of natural gas, e.g. by gas reforming and shift  
15 technology for preparation of a mixture consisting of hydrogen and carbon dioxide. These components are then separated, after which hydrogen may be used in a number of applications, such as electricity generation, heat generation and in different types of transportation. Hydrogen may also be mixed with natural gas to produce hytane, a fuel for domestic and industrial energy users. Carbon dioxide has  
20 industrial applications but may also be deposited after compression to a desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.

Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of  
25 the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen that is made by splitting water through electrolysis and compressed to typically 700 bar. Liquid hydrogen is being considered for heavier transport like ships and trains. Unfortunately, electrolysis has been calculated to be at least twice as costly as producing hydrogen by reforming natural gas. These  
30 calculations include costs of separation and liquefaction of coproduced CO<sub>2</sub> and payment of tariffs for deposition of CO<sub>2</sub> in underground reservoirs. Another

complicated issue with water electrolysis is calculation of the greenhouse effect, as most electricity is still produced from hydrocarbons with significant emission of CO<sub>2</sub> to the atmosphere. Therefore, producing hydrogen from natural gas with CO<sub>2</sub> storage is a significantly better option.

- 5 There is a general need to improve hydrogen production processes.

## SUMMARY OF INVENTION

According to a first aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons;  
10 performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate  
15 streams of hydrogen, carbon dioxide and a rest gas; and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the reforming process, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process; wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and  
20 more preferably at least 90%.

Preferably, the one or more reforming processes comprise an autothermal reforming process.

Preferably, the one or more reforming processes comprise a partial oxidation reforming process.

- 25 Preferably, the reforming process comprises a gas heated reforming process.

Preferably, the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

- 30 Preferably, the method further comprises: optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas;

and optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; wherein the pre-reforming process comprises: optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

Preferably, the hydrogen separation process comprises: inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane; outputting hydrogen from the permeate side of the Palladium membrane; and outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

Preferably, the hydrogen separation process comprises a PSA process.

Preferably, the rest gas that is recycled is fed back into the autothermal reforming process and/or another reforming process, such as a partial oxidation reforming process.

Preferably, the rest gas that is recycled is fed back into the water-gas-shift process.

Preferably, the rest gas that is recycled is fed back into the hydrogen separation process.

Preferably, the feed gas is natural gas.

Preferably, the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.

Preferably, the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

Preferably, the autothermal reforming process is supplied with oxygen from an air separation unit.

Preferably, the water-gas-shift process is conducted in one water-gas-shift reactor; wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C,

and/or at about 300 °C; and wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

Preferably, the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

- 5 Preferably, no additional steam is added between the reforming processes and the water-gas-shift process.

Preferably, the method further comprises operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

- 10 Preferably, water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

Preferably, water is not separated from the shifted gas before the hydrogen separation process.

- 15 Preferably, the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

Preferably, the carbon dioxide separation process is conducted cryogenically.

- 20 Preferably, the method further comprises generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

According to second aspect of the present invention, there is provided a hydrogen production plant arranged to perform the method of the first aspect.

According to third aspect of the present invention, there is provided an ammonia production plant arranged to perform the method of the first aspect.

25

## BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows a reforming process comprising a gas-heated reforming process and an autothermal reforming process.



Figure 2 shows a configuration of a hydrogen production process.

Figure 3 shows a configuration of a hydrogen production process according to an embodiment.

5 Figure 4 shows a configuration of a hydrogen production process according to an embodiment.

Figure 5 shows a configuration of a hydrogen production process according to an embodiment.

Figure 6 shows a configuration of a hydrogen production process according to an embodiment.

10 Figure 7 shows a configuration of a hydrogen production process according to an embodiment.

Figure 8 shows a configuration of a hydrogen production process according to an embodiment.

15 Figure 9 shows a configuration of a hydrogen production process according to an embodiment.

Figure 10 comprises Table 1.

Figure 11 comprises Table 2.

Figure 12 comprises Table 3.

Figure 13 comprises Table 4.

20 Figure 14 comprises Table 5.

Figure 15 comprises Table 6.

Figure 16 shows a configuration of an ammonia production process according to an embodiment.

## 25 DETAILED DESCRIPTION OF EMBODIMENTS

A known method for the production of a CO<sub>2</sub>-rich gas stream and a H<sub>2</sub>-rich gas stream comprises the following steps:

a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas, also referred to as syngas, under supply of an O<sub>2</sub>-containing gas. Syngas mainly comprises H<sub>2</sub> and CO;

b) the gas stream from a) is shifted so as to produce a mixture of H<sub>2</sub> and CO<sub>2</sub> by reaction with H<sub>2</sub>O;

c) CO<sub>2</sub> is separated from the gas stream from b) in a CO<sub>2</sub> separation unit;

d) H<sub>2</sub> is separated from the CO<sub>2</sub>-depleted gas from c) in a H<sub>2</sub> separation unit.

The above method describes the basic principles behind the production hydrogen from natural gas with separation of hydrogen and CO<sub>2</sub>.

Known techniques combust the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> as fuel. If a relatively high percentage of hydrogen has not been separated, then a significant amount of hydrogen will be wasted in this fuel. Furthermore, the combustion of any accompanying carbon containing species in the fuel produces uncaptured CO<sub>2</sub>.

Most hydrogen producing processes from natural gas known in the art rely on the use of a steam reformer, and in some instances on an autothermal reformer (ATR), i.e. using an autothermal reactor, or a partial oxidation reactor (POX). However, use of a gas-heated-reformer (GHR) in combination with an autothermal reformer is considerably more energy efficient.

Production and perspectives on syngas production has been described by J. R.

Rostrup-Nielsen in Catalysis Today, volume 18, pages 305-324, 1993, and in volume 71, pages 243-247, 2002. There are several types of reformers for production of synthesis gas comprising steam reforming, autothermal reforming and partial oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.

Separation of CO<sub>2</sub> is frequently done by an amine washing process, a carbonate process, and sometimes by using a physical sorbent like methanol or ethers; or simply by washing with water.

5 Hydrogen may be separated from a hydrogen containing gas mixture by use of a pressure swing absorption/adsorption (PSA) processor. In some implementations of PSA processes by a PSA reactor, the PSA reactor is a large and costly part of the hydrogen plant. PSA processes may also result in CO<sub>2</sub> being released at low pressure, e.g. atmospheric pressure, and so there is a subsequent need for compression and cooling. Still, it can be feasible to use PSA for some hydrogen  
10 production plants.

Embodiments provide new and particularly advantageous implementations of systems for producing hydrogen from natural gas. Hydrogen production may be the main purpose of the system. However, embodiments also include using at least some of the hydrogen, or all the hydrogen, to produce ammonia. Ammonia is an  
15 alternative energy carrier to compressed or liquefied hydrogen. In addition to the production of fertilizers and some chemicals, ammonia may be used as fuel in energy, transportation, maritime and offshore markets.

Embodiments also provide a high carbon capture efficiency that may be at least 90% of the carbon in the feed gas, and preferably at least 97%.

20 Although embodiments may separate CO<sub>2</sub> by using an amine washing process, or other process, embodiments preferably use cryogenic separation to separate CO<sub>2</sub>. That is to say, the gas stream is cooled to a temperature, and at a pressure, where CO<sub>2</sub> is liquefied.

Cryogenic separation of CO<sub>2</sub> has in the known art been assumed to be  
25 disadvantageous as a smaller fraction of CO<sub>2</sub> is separated. However, embodiments avoid this disadvantage by providing novel process design. CO<sub>2</sub> is obtained directly in a liquid form, i.e. ready for transportation to a deposition site.

Embodiments advantageously re-use the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> in the hydrogen production system. This improves the carbon capture efficiency  
30 of the system.

Embodiments include using a Palladium membrane (Pd-membrane) to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons. One advantage is that hydrogen is obtained with high purity; that may be greater than 99% and is often greater than 99.9%. Another advantage is that the gas containing CO<sub>2</sub> that does not pass through the membrane, which is referred to as the retentate, is at an elevated pressure, typically above 10 bar, more typically between 20 and 40 bar, but sometimes even at pressures up to 100 bar. It is even preferred that the Pd-membrane operates at an elevated temperature; 200-400 °C, or in a narrower range above or around 300 °C, so that it is well suited for operation down-stream of the water-gas-shift (WGS) reactor or reactors.

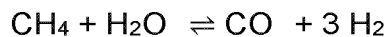
Embodiments also include using a PSA process, or PSA processes, to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons.

Embodiments include receiving a supply of natural gas, or more generally a hydrocarbon containing gas from any source. The natural gas may be cleaned and pre-treated in a suitable manner so that the gas feed mainly comprises methane after treatment. Such cleaning typically comprises sulfur removal, for example by one or more ZnO absorbers. Sometimes heavy metals, typically Hg, are also removed. The pre-treatment may also comprise a pre-reforming process whereby higher hydrocarbons, such as ethane, are converted by steam to methane and CO<sub>2</sub>.

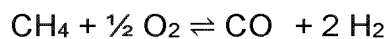
The reforming process according to embodiments may take place at a pressure within the interval 10 to 200 bar.

The water-gas shift reaction according to embodiments may take place in one or more shift reactors. Steam may be supplied to the shift reactor, but the shift reactor may also be operated without supply of steam as steam already may have been introduced into the reformer. At the outlet of the shift reactor, the carbon content may comprise CO<sub>2</sub> and methane. CO<sub>2</sub> may be about 2% to about 5% by volume or higher. Methane may be about 2% to about 5% by volume or higher.

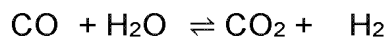
The following chemical reactions may take place during production of synthesis gas and hydrogen by reforming of natural gas:



1. Steam reforming



2. Partial oxidation



3. Shift reaction

The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by partial oxidation in an autothermal reformer.

5 In a steam reformer (SR) natural gas (i.e. methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer consists of many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range  
10 from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer is approximately 950 °C. The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the produced stream is from 2.7 to 3.0.  
15 Synthesis gas produced from a steam reformer may contain approximately 3% methane by volume.

Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR, natural gas (methane) is fed together with oxygen or air into a combustion chamber. The energy which is required to operate  
20 the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions may be driven to equilibrium over a catalyst bed before the synthesis gas leaves the reactor at approximately 1000-1050 °C. The size of such a unit could  
25 be a height of 10-15 meters and a diameter of 5-6 meters. A typical ratio of steam:carbon in the output gas is from 0.6 to 1.4. The ratio of hydrogen to carbon monoxide in the output gas is lower than 2. Typical methane slip, i.e. amount of

unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR.

A further option for reforming natural gas is a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed.

- 5 The exit temperature for a POX is higher than for a typical ATR, sometimes significantly higher and it may be above 1200 °C. POX is often characterized by no steam added to the feed. A catalyst might be included, thus defining a catalytic partial oxidation (CPOX) reactor.

- 10 Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. In combined reforming, SR is operated at milder conditions (i.e. lower outlet temperature), which leads to a high methane slip. The residual methane is then reacted in the ATR. The ratio of  
15 steam:carbon is in the area 1.8-2.4, with a ratio of hydrogen to carbon monoxide in the product gas higher than 2.

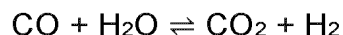
- From the above, it is clear that the conventional reformer unit has a very large footprint (SR), and that the exit gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB)  
20 that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting. It has been found, however, that a more efficient process is experienced if the hot output gas is used to reform part of the natural gas before it enters the autothermal reformer. This combination of ATR with oxygen and a gas-heated-reformer (GHR) has been tested in a  
25 demonstration unit for production of methanol. This development originates in ICI in the 1980s to completely remove the traditional steam reformer in their Leading Concept Methanol (LCM) process.

- Figure 1 shows an efficient reforming process that may be used in embodiments. The hot exit gas from the reformer is used to reform part of the natural gas before it  
30 enters the autothermal reformer. Instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the

catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR 1, then the partially reformed gas in stream 21 passes through the ATR 2, and finally the reformed gas in stream 22 passes through the heating side of the GHR 1 to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only moderate further cooling before the water-gas-shift process (WGS).

Although embodiments include the reforming process shown in Figure 1, embodiments also include alternatively using any other type of reforming process. For example, embodiments include only using an autothermal reformer or only using a gas-heated-reformer.

After reforming of the natural gas and cooling, the gas mixture is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and some CH<sub>4</sub>. Between these components there is an equilibrium relation given by the stoichiometric equation:



This reaction is called the water-gas-shift (WGS) reaction, and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors may be used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. The catalyst in the first step may be based on chromium/iron, whereas the catalyst in the second step may be a copper/zinc catalyst. In the shift unit CO and H<sub>2</sub>O are reacted to form CO<sub>2</sub> and H<sub>2</sub>, and in known techniques it is often a

requirement that the mentioned reaction is driven to the right to the highest possible degree, so that as little CO as possible is present in the gas mixture exiting the shift unit. A low content of CO in the mentioned gas mixture again may give a high purity of the H<sub>2</sub>-rich gas stream out of the separation unit.

- 5 In known techniques the shift reactor is operated so that the ratio H<sub>2</sub>O:CO to the shift reactor is high, e.g. equal to 10:1, so that there is a high conversion of CO.

Embodiments may differ from such techniques by optimizing the processes in a WGS reactor in conjunction with a hydrogen separation processes by a Palladium membrane. The efficiency of a Pd membrane may be improved by operating at a  
10 certain elevated temperature. Preferably, only a high- or medium- temperature WGS is therefore applied before the membrane. A low-temperature WGS may also be used after the membrane and the shifted gas partly recycled, i.e. fed back into one of the earlier processes in the hydrogen production process.

In a preferred embodiment, the temperature of the WGS process is determined in  
15 dependence on an operating condition of the Pd-membrane. For example, the temperature of the WGS process may be set substantially at the operating condition of the Pd-membrane, e.g. about 300 °C, thereby avoiding any need for heat exchange between the two units. It is not necessary for the WGS process to be  
20 operated in a way that maximizes the conversion of CO because the rest gas is recycled back into the earlier processes. Embodiments include no additional steam being added before the WGS reactor. When the Pd-membrane is operated at about 300 °C, a Cu-based catalyst may be used.

If a different to Pd-membrane hydrogen separation process is used, like PSA, it still might be feasible to operate only one WGS reactor, e.g., an isothermal shift reactor.  
25 Ultra-high conversion of CO is not always needed, and can be rectified by recycle of rest gas.

Gases in the mixture after the shift reactor, or the shift reactors, can be separated more or less completely based on the different properties of the gas molecules. The most common techniques are absorption, adsorption and cryogenic distillation.  
30 CO<sub>2</sub> is an acid gas, and the most widely used method to separate the mentioned gas



from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by  
5 altering the composition of the liquid or by altering pressure and/or temperature. For separation of CO<sub>2</sub>, aqueous solutions of alcoholamines can be used. The absorption takes place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO<sub>2</sub> from the amine phase in the stripping unit, stripping steam is usually  
10 used. If the partial pressure of CO<sub>2</sub> in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO<sub>2</sub> can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar. Other absorption technologies rely on alternative physical liquid absorbents like methanol at reduced temperature.

15 Embodiments preferably separate hydrogen from the gas output from the WGS reactor using a membrane. In particular, a Pd-film membrane may be used. By the use of one or more semipermeable or dense membrane units, molecules of different size and different properties can be made to permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture from  
20 the WGS reactor, membranes can be selected where H<sub>2</sub> permeates rapidly, whereas CO<sub>2</sub> permeates slowly or not at all, so that separation of the different gas components is achieved. The membrane may be a Palladium membrane.

The driving force over the membrane is the difference in partial pressure, i.e. of hydrogen between the process gas (which is the received gas on the retentate side  
25 of the membrane) and gas on the permeate side of the membrane. As hydrogen in many cases is required at an elevated pressure, a way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. Although embodiments include using a sweep gas, this is optional and embodiments  
30 also include not using a sweep gas.

Embodiments may alternatively use a combination of solid membranes and liquid membranes through which there is a rapid permeation of CO<sub>2</sub>, while H<sub>2</sub> is kept back.

Embodiments may alternatively use PSA to separate hydrogen from the gas output from the WGS reactor. PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material. In the present mixture of gases, CO, CO<sub>2</sub> and CH<sub>4</sub> are adsorbed, letting the hydrogen pass through at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit. Alternatively, the temperature can swing instead of the pressure.

Capturing CO<sub>2</sub> by refrigeration is a cost and energy efficient method compared to other technologies. In known techniques, electricity may be used to drive the compressors. The main challenge has been that only in the order of 90% of CO<sub>2</sub> is captured this way, or perhaps 93% by optimizing conditions. In addition, there are some carbon losses from unconverted CO and CH<sub>4</sub> and these reduce the overall carbon capture to 90% or below. Specific advantages of using cryogenic CO<sub>2</sub> separation are that the product is directly in the liquid form needed for deposition and no additional compression is required.

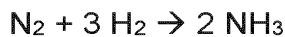
Embodiments include separating out CO<sub>2</sub> and then depositing the separated CO<sub>2</sub>. Large amounts of CO<sub>2</sub> can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water geological reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO<sub>2</sub> gas has to be brought to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO<sub>2</sub> gas can be separated from the H<sub>2</sub>/CO<sub>2</sub> mixture at an elevated pressure, significant compression work can be avoided.

Embodiments may allow a selection to be made between collecting hydrogen and CO<sub>2</sub> at the high (process) pressure. A hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen, is needed for storage and in

transportation applications. As it is more demanding to pressurize hydrogen than CO<sub>2</sub>, separation technologies that provide hydrogen at high pressure are sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen-permeable membrane.

- 5 Embodiments include using an air separation unit (ASU) to generate oxygen. The oxygen may be supplied to an autothermal reactor, ATR, or a partial oxidation reactor (POX), used in the reforming process. The ASU may cryogenically separate air into oxygen and a gas mixture that mostly comprises nitrogen. Embodiments include using the nitrogen, from the ASU, and hydrogen, from the membrane separator, to  
10 generate ammonia.

Combining nitrogen with hydrogen allows production of ammonia, NH<sub>3</sub>, according to the reaction:

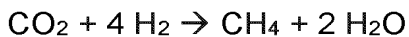


- Ammonia can be used as an environmentally friendly fuel as long as any CO<sub>2</sub>  
15 generated during production is captured. The benefits of using ammonia include ease of transportation and handling. Liquid ammonia can be stored in vessels at about 17 bar.

The ammonia process is favored by high pressures, and an elevated temperature is needed for sufficient reaction rate.

- 20 A known production technique of ammonia is from natural gas, or sometimes from higher hydrocarbons, by reforming the gas to syngas that is shifted to mostly hydrogen and CO<sub>2</sub>. Using air in the process stream, like applying an ASU, gives a mixture of hydrogen, nitrogen, water and CO<sub>2</sub> after shift conversion. The shift reaction is frequently carried out in two steps, high-temperature and low-temperature  
25 shift, to convert CO to low levels. Before the ammonia synthesis, water is knocked out and CO<sub>2</sub> removed by elaborate means. Further, residual CO and CO<sub>2</sub> has to be removed as they are poisons for the catalyst, and this is done by methanation;





The ammonia synthesis loop is also known as Haber-Bosch synthesis. The reaction is run over a catalyst that typically is promoted magnetite. Single pass conversion over the catalyst is around or below 20% and, therefore, significant recycle is  
5 required. The pressure is in the range 60-200 bar depending on process design. This is significantly higher than reforming and shifting natural gas that takes place in the pressure range 20-35 bar. On the other hand, the reaction pressure to make ammonia is significantly lower than the 300-700 bar required for hydrogen as energy  
10 carrier. Reaction temperature is ca. 450 °C. There have been many types of design of ammonia plants during the last 60 years. One option that has been explored is to produce hydrogen from steam reforming combined with PSA, and combined this hydrogen with nitrogen from an ASU-unit. Such a plant, however, is not favorably designed for separating a pure CO<sub>2</sub>-stream for storage.

Embodiments are described in more detail by the following examples of  
15 embodiments and figures.

Process simulations using the program UniSim are based on natural gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher hydrocarbons, 1.5% CO<sub>2</sub> and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. The natural gas flow is 4625 kg/h; 246 kmol/h. Hydrogen  
20 specification is > 99.97 mol% for fuel cells, and specification for CO<sub>2</sub> is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C.

A number of process schemes are analyzed. These include one comparative example and a number of implementations of embodiments, four of which are summarized in Table 1 in Figure 10. The schemes vary in WGS temperature, use of  
25 Pd-membrane or PSA for hydrogen separation, use of amine solvents or cryogenic CO<sub>2</sub> separation, as well as the position of water condensation.

The membrane may be always operated at a preferable temperature for permeation of hydrogen through the membrane. For example, the membrane may be operated at 300 °C. However, the WGS may be operated at 256 °C for highest CO conversion,

but at 300 °C when the shifted gas is directly introduced to the membrane; i.e. without any heat exchange and water condensation.

The conditions of Embodiment Example 2 are applied in Embodiment Examples 5-7, where recycle of rest gas is used.

- 5 The following reasonable assumptions are made, but without fixing these conditions: in amine cases, it is assumed that 100% of inlet CO<sub>2</sub> is removed by the unit; in membrane cases, 93% H<sub>2</sub> separation is assumed; produced H<sub>2</sub> from the membrane unit is at 3 bar and compressed to 350 bar for export; the final CO<sub>2</sub> stream is delivered at -26.2 °C at 16 bar. It is understood that the applied conditions are
- 10 reasonable for comparing different process schemes, but that a variety of other conditions can be used; e.g. for different natural gas compositions, requirements for delivery of hydrogen and CO<sub>2</sub>, and site specific conditions like possibilities for integration with other process units and the availability of electricity from the grid.

### Comparative Example

- 15 Figure 2 is a process flow sheet showing production of hydrogen and CO<sub>2</sub> by combination of ATR 2 and GHR 1 according to a comparative example to embodiments.

The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen stream 101 is optionally added

20 to the pretreated natural gas 41 as stream 103 and fed to the optional pre-reformer 4. The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen 51 from an air separation unit (ASU) 5 is added to the ATR 2. The ASU separates cryogenically air 53 into oxygen 51 and

25 nitrogen 52, sometimes also producing noble gases like argon. It should be understood that embodiments include any other means for producing oxygen, or air enriched in oxygen, such as by using vacuum or pressure swing adsorption, or by using a membrane.

- The produced syngas 12 is shifted to increase the content of hydrogen and CO<sub>2</sub> in
- 30 one or more shift reactors 6, i.e. water-gas-shift reactor(s) 6, to produce the shifted

gas 61. Steam may be added to the gas mixture before the gas mixture is input into the shift reactor(s) 6. The addition of steam increases the efficiency of the shift reaction. The shifted gas 61 is subsequently cooled in the condenser 7 to remove its water content 72, thus obtaining dry shifted syngas 71. Amine type separation

5 process 8 separates CO<sub>2</sub> 81 from the shifted gas, and the CO<sub>2</sub> 81 is then compressed 9 and liquefied. The produced CO<sub>2</sub> 91 may be stored at site, shipped for permanent storage or directly injected into a geological formation for storage.

Hydrogen 101 is separated in the process 10 by the known technique of pressure-swing absorption/adsorption (PSA), that separates the hydrogen from the gas 82 that  
10 has already been depleted of CO<sub>2</sub> by the process 8. The separate outputs from the process 10 are hydrogen 101 and a rest gas 102. The rest gas 102 contains remnants of CO and CH<sub>4</sub> together with unseparated CO<sub>2</sub> and hydrogen. The energy in the rest gas is utilized for fuel in fired heater(s) for preheating of feed gases natural gas and water/steam. Finally, the produced hydrogen 101 is compressed 11 to give  
15 hydrogen 111 at 340 bar.

The simulations show that production of 100 kNm<sup>3</sup>/hr hydrogen requires 35.7 kNm<sup>3</sup>/hr of NG and 16.7 kNm<sup>3</sup>/hr of oxygen. 622 tons of CO<sub>2</sub> is captured each year, assuming that the PSA rest gas 102 is used for combustion and the exhaust gas CO<sub>2</sub> emitted to the atmosphere. This gives a CO<sub>2</sub> capture efficiency of 95.4%. Electric  
20 power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

### Embodiment example 1

Figure 3 shows a method for production of hydrogen from natural gas with separation  
25 of CO<sub>2</sub> according to embodiment example 1. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

30 The present embodiment differs from the above-provided comparative example in that hydrogen separation is performed before CO<sub>2</sub> separation. After the WGS

process, the shifted gas enters a hydrogen separation vessel that comprises a Pd-membrane 12. The hydrogen separation vessel may receive the output gas from the WGS reactor on the retentate side of the Pd-membrane. Hydrogen passes through the Pd-membrane to reach a permeate side of the Pd-membrane. The hydrogen on the permeate side of the Pd-membrane is output as stream 121. The gas stream output from the retentate side of the Pd-membrane is hydrogen-depleted gas 122.

The hydrogen stream 121 is sent to compressor 11 while the hydrogen-depleted gas stream 122 is depleted of water 72 in the condenser 7. The dried gas 73 is then input into the amine separator 8 that outputs CO<sub>2</sub> stream 81 and a rest gas 83.

CO<sub>2</sub> stream 81 is compressed 9, and the CO<sub>2</sub> depleted rest gas 83 may be used for providing energy in fired heater(s).

Advantageously, the use of a Pd-membrane separator for separating hydrogen as the subsequent process to the WGS process allows the hydrogen separation process to be performed particularly efficiently and effectively. In particular, the temperature and/or pressure conditions in the WGS reactor may be selected in order to substantially optimize the operating conditions of the membrane separator (e.g. to maximize the separation of hydrogen in the membrane separator).

### **Embodiment example 2**

Figure 4 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 2. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane and water condensation 7 may be as described with reference to Figure 3 with corresponding reference signs.

A difference between embodiment example 2 and embodiment example 1 is that the amine unit 8 of embodiment example 1 is replaced with cryogenic separation 13 of CO<sub>2</sub> 131 from the dried gas 73, giving the rest gas 132 for use in fired heater(s).

### **Embodiment example 3**

Figure 5 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 3. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with  
5 corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. This embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as  
10 stream 71. In addition, reducing the water concentration before the membrane unit may advantageously increase the hydrogen concentration and may protect materials in the membrane unit.

The use of water condenser 7 on the gas output from the retentate side of the membrane separator 12 is optional.

15 CO<sub>2</sub> 81 is removed in an amine unit 8 leaving an energy rich rest gas 84.

#### **Embodiment example 4**

Figure 6 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 4. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming  
20 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

The present embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such a  
25 configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as stream 71.

CO<sub>2</sub> 131 is removed in the cryogenic unit 13 leaving an energy rich rest gas 132.

A comparison of the comparative example and embodiment examples 1-4 is provided below.



A comparison of performance of the comparative example and embodiment examples 1, 2, 3 and 4 is listed in Table 2 in Figure 11. There are, in addition, differences in investment and operating costs (i.e. CAPEX and OPEX). As to the investment costs, prices from vendors show that for hydrogen separation, PSA is considerably more costly than using a Pd-membrane, and that for CO<sub>2</sub> separation, using amine is significantly more costly than cryogenic separation. In addition, the footprints of PSA and amine are much larger than for Pd-membrane and cryogenic CO<sub>2</sub> separation.

Using a Pd-membrane, as in embodiment examples 1-4, is advantageous due to lower cost, smaller footprint and a higher hydrogen recovery factor than the comparative example. Note from the H<sub>2</sub> recovery factor that only 7% of the hydrogen in the shifted gas is lost in embodiment examples 1-4, compared to 14% in the comparative example. The percentage of carbon captured is above the 95% mark for embodiment examples 1 and 3, which is fully acceptable for most projects, although these still use amine separation of CO<sub>2</sub>. The amine separation in these two embodiments is, however, significantly simpler than in the comparative example, due to the more than 3-fold higher concentration of CO<sub>2</sub> in the inlet gas. Other factors to be considered are the conversion in the WGS (see Table 2 in Figure 11), and differences in how water is condensed (see Table 1 in Figure 10 as well as the figures).

Known techniques are based on the assumption that a high conversion of CO in the WGS reactor results in better system performance with regard to hydrogen and CO<sub>2</sub> recovery. However, test of embodiments show that the performance of the separation technologies is more dominant on the overall system performance. Accordingly, operating the WGS at 300 °C is advantageous.

There is no condensation of water and heat exchange after WGS and before the Pd-membrane in Embodiment Examples 1 and 2, in contrast to Embodiment Examples 3 and 4. The discussed advantages are summarized in Table 3 in Figure 12. It follows that using a Pd-membrane is preferable compared the comparative example, and that there is no need to adjust temperature and knock out water directly after WGS.

### **Embodiment examples 5-7**

Figure 7 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment Examples 5-7.

The processes in embodiment Examples 5-7 may be substantially the same, or identical, to Embodiment Example 2 except that the rest gas 132 is recycled to the ATR 2.

The oxygen feed 51 may be adjusted to secure a constant exit temperature from ATR of about 1020 °C. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. The separation of hydrogen by a Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation 13 may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest gas 132 is used as recycle-gas to the ATR 2. The processes in the ATR 2 are therefore adapted so that the rest gas can additionally be received by the ATR 2.

The difference between Embodiment Examples 5-7 is in the amount of rest gas that is recycled, which is detailed in Table 4 in Figure 13.

### **Comparison of Embodiment Examples 2 and 5-7**

In Table 4 in Figure 13, Embodiment Examples 5-7, with recycle of rest gas, are compared to Embodiment Example 2. Although Embodiment Example 2 shows good performance, as seen in Table 3 in Figure 12, it is desirable to improve the efficiency of CO<sub>2</sub> capture and the carbon capture fraction. Embodiments achieve this by recycling at least part of the rest gas to the reformer section. The results outlined in Table 4, in Figure 13, show a surprising effect in that much better performances are reached. Hydrogen production increases, with a recovery of 99% for Embodiment Example 7 (90% recycle), compared to 93% H<sub>2</sub> recovery for Embodiment Example 2 as defined in Table 2 in Figure 11; hydrogen loss is reduced from 7% to 1%. Simultaneously, the carbon capture increases from 90% in Embodiment Example 2 to 99% in Embodiment Example 7, the best performance of all examples.

When the production and separation efficiencies increase, more oxygen is needed in the ATR and less fuel gas is available for heat generation. The advantages summarized in Table 5, in Figure 14, indicates that a high degree of recycle is preferable. Probably more important is that a superior carbon capture fraction, as in  
5 Embodiment Example 7, is considered a decisive advantage in many hydrogen projects.

### Embodiment Example 8

Figure 8 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 8 which may be identical to Embodiment  
10 Example 2 except that the rest gas 133 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the WGS 6. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as  
15 described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest gas 133 is used as recycle-gas to the WGS 6. Process simulations have been made for recycle of 50%, 80% and 90% of rest gas to WGS. However,  
20 embodiments include using any feasible recycle ratio of the rest gas.

### Embodiment Example 9

Figure 9 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 9 which may be identical to Embodiment  
25 Example 2 except that the rest gas 134 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the membrane unit 12. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of  
30 hydrogen by the Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The

only difference is that the rest gas 134 is used as recycle-gas to the membrane unit 12. Process simulations have been made for recycle of 50%, 80% and 90% of rest gas to the Pd-membrane. However, embodiments include using any feasible recycle ratio of the rest gas.

## 5    **Embodiment Example 10**

Embodiment Example 10 is identical to Embodiment Examples 5-7 except that the oxygen feed 51 is kept constant compared to Embodiment Example 2. This reduces the exit temperature from the ATR 2 from 1020 °C to, respectively, 1008 °C, 999 °C, 989 °C and 974 °C for 30%, 50%, 80% and 90% recycle.

## 10   **Comparison of Embodiment Examples 2, 6, 8, 9 and 10**

Table 6, in Figure 15, summarizes 80% recycle of rest gas from CO<sub>2</sub> separation compared to no recycle. The recycle is to the ATR, WGS and Pd-membrane respectively. For recycle to ATR, the oxygen feed has been increased in Embodiment Example 6 to keep the exit temperature constant. The following  
15    surprising advantageous effects are found:

- Hydrogen production increases significantly for all recycle cases.
- Carbon capture rate increases significantly for all recycle cases.
- Very high capture rates are obtained when recycle is to ATR or WGS.
- Recycle to ATR without increasing oxygen flow is beneficial.
- 20    • More energy for fired heater is available when recycle is to Pd-membrane.

## **Embodiment Example 11**

Figure 16 shows a system according to Embodiment Example 11.

Embodiment Example 11 is directed towards producing ammonia 141 and is similar to all previous Embodiment Examples in that a Pd-membrane 12 is used to separate  
25    hydrogen, the syngas is produced by a combination of GHR 1 and ATR 2, and there is a WGS reactor(s) 6.

In the present embodiment, nitrogen 52, from the ASU 5, is combined with hydrogen, from the membrane separator 12, in an ammonia synthesis unit 14. The hydrogen

supplied to the ammonia synthesis unit 14 may be either hydrogen stream 121 or the compressed hydrogen stream 111.

A preferred implementation of the present embodiment is shown in Figure 16. This is similar to Embodiment Example 8 and has corresponding reference signs. However, 5  
embodiments also include alternatively generating the hydrogen supply using any of the other Embodiment Examples described herein, and using any recycle ratios of rest gas.

Advantages of using systems according to the present embodiment for the production of ammonia include, but are not limited to, efficient natural gas reforming 10  
by using GHR/ASU, one-step WGS reaction, hydrogen separation at the same temperature as WGS, ease of separating CO<sub>2</sub> by cryogenic cooling, high hydrogen productivity and low CO<sub>2</sub> emission by recycle of rest gas, and low content of inerts in the ammonia synthesis loop.

### **Embodiment Example 12**

15 The present embodiment is directed towards providing performance gains by recycling the rest gas that remains after the hydrogen and CO<sub>2</sub> separation processes.

In the present embodiment, the hydrogen separation process may be performed before the CO<sub>2</sub> separation process, and the rest gas is therefore the gas remaining after the CO<sub>2</sub> separation process. The present embodiment also includes an 20  
alternative implementation in which the CO<sub>2</sub> separation process is performed before the hydrogen separation process, and the rest gas is therefore the gas remaining after the hydrogen separation process.

The rest gas may be fed back into one or more of any of the processes performed in the hydrogen production process. For example, the rest gas may be fed back into 25  
one or more reforming process, water-gas-shift process, hydrogen separation process and CO<sub>2</sub> separation process.

All of the rest gas may be recycled by feeding it back into one or more of the processes performed in the hydrogen production process. Alternatively, only a portion of the rest gas may be recycled. The portion of the rest gas that is recycled 30  
may be at least 50%, preferably at least 80%, and more preferably at least 90%.

In the present embodiment, any reforming process may be used. In particular, the reforming process may only comprise an autothermal reforming process.

In the present embodiment, any hydrogen separation process and CO<sub>2</sub> separation process may be used. In particular, the hydrogen separation process may be a PSA process. The CO<sub>2</sub> separation process may be a cryogenic process.

In the present embodiment, the hydrogen separation process is not restricted to being performed before the CO<sub>2</sub> separation process. Embodiments include the CO<sub>2</sub> separation process alternatively being performed before the hydrogen separation process and the rest gas being the remaining gas following the hydrogen separation process. Some, or all, of the rest gas may be recycled as described above.

The embodiments presented throughout the present document provide advantageous methods and systems for the production of hydrogen and/or ammonia. In particular, the use of a Pd-membrane to separate hydrogen immediately downstream of a WGS reactor has a surprising synergistic effect. Contrary to known techniques, the WGS reactor may be operated at substantially the same temperature as the Pd-membrane. The WGS reactor may be operated under conditions that are more preferable for the effective operation of the Pd-membrane and this can substantially improve the overall efficiencies and effectiveness of the system.

In a particularly preferred implementation according to an embodiment, the hydrogen separation process uses a hydrogen separation device as disclosed in the published patent application WO2020/012018A1, the entire contents of which are incorporated herein by reference. The hydrogen separation device disclosed in WO2020/012018A1 uses Pd-membranes to separate hydrogen from a gas mixture. The operational capabilities of the hydrogen separation device disclosed in WO2020/012018A1 result in it being particularly suitable for use in the hydrogen and/or ammonia production processes according to embodiments.

Other particularly advantageous techniques that may be used in methods and systems according to embodiments are the recycling of the rest gas directly to the Pd-membrane separator and/or water gas shift (WGS) reactor.

Embodiments include a number of modifications and variations to the above described techniques.

Embodiments may use a Pd-membrane separator 12 to separate hydrogen from shifted gas. Optionally, a sweep gas may be used on the permeate side of the membrane. The sweep gas may be steam. The steam may be at an elevated total pressure above 5 bar, preferably above 10 bar.

- 5    Embodiments include the use of a water separator, such as a condenser, in between the Pd-membrane separator 12 and the hydrogen compressor 11 to separate hydrogen from the used sweep gas.

Embodiments also include optionally using a sweep gas on the retentate side of the membrane.

- 10   In embodiments, a) sulfur may be removed from the feed gas, b) the feed gas may be saturated with water, c) hydrogen may optionally be added to the gas stream before pre-reforming the gas that has been subject to treatments a and b, d) the gas from c may be reformed by a combination of gas-heated reforming and autothermal reforming, e) the reformed gas may be subjected to water-gas-shift to give a shifted  
15   gas, f) hydrogen may be separated from the shifted gas using a Pd-membrane, g) carbon dioxide may be separated from the shifted gas that has been subject to treatment f, h) the separated hydrogen is optionally compressed and liquefied, i) the separated carbon dioxide is optionally compressed and liquefied.

- 20   In embodiments, at least part of the rest gas from separating hydrogen and carbon dioxide may be recycled.

In embodiments, the portion of the rest gas that is recycled may be more than 50%, preferably around 80%, more preferably at least 90%. Embodiments include all of the rest being recycled.

- 25   In embodiments, the rest gas that is recycled may be fed back into the gas-heated reforming process.

In embodiments, the rest gas that is recycled may be fed back into the autothermal reformer, the water-gas-shift reactor(s) and/or the Pd-membrane.

In embodiments, the feed gas may be natural gas.

- 30   In embodiments, the feed gas may be a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.

In embodiments, the gas-heated reformer may be heated by the exit gas from an autothermal reformer.

In embodiments, the exit temperature of the reformed gas from the gas-heated reformer may be in the range 400-800 °C, preferably 450-700 °C, more preferably  
5 540-600 °C.

In embodiments, the autothermal reformer may be supplied with oxygen from an air separation unit.

In embodiments, the autothermal reformer may be supplied with oxygen or oxygen enriched air from a membrane air separation unit.

10 In embodiments, the water-gas-shift reaction may be conducted in a high-temperature-shift and a low-temperature shift reactor.

In embodiments, the water-gas-shift reaction may be conducted in one reactor.

In embodiments, the water-gas shift reactor may be operated at a temperature between 200 and 300 °C, preferably between 240 and 270 °C.

15 In embodiments, the water-gas shift reactor may be operated at a temperature between 270 and 330 °C, preferably between 290 and 310 °C, most preferably at about 300 °C.

In embodiments, no additional steam may be added between the reformer and the WGS-reactor.

20 In embodiments, the water-gas shift reactor may utilize a Cu-based catalyst.

In embodiments, the CO conversion in the WGS reactor may be at least 90%, but below 98%, more preferably below 96%.

In embodiments, hydrogen may be separated before CO<sub>2</sub> is separated from the shifted gas.

25 In embodiments, the WGS and the Pd-membrane may be operated at about the same temperature.

In embodiments, water may be separated after the Pd-membrane and not before the membrane.



In embodiments, the Pd-membrane may be operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

5 In embodiments, carbon dioxide may be separated cryogenically. The carbon dioxide may be deposited in a geological reservoir.

In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by a nearby processing plant.

10 In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by electricity from the grid and/or electricity from renewable energy source(s).

In embodiments, nitrogen may be produced by the air separation unit.

In embodiments, nitrogen and hydrogen may be used to produce ammonia. In embodiments, methanisation may be substantially avoided in the ammonia synthesis.

Embodiments include the following numbered clauses:

15 1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

20 performing reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide, wherein

the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process, and

25 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

30

performing a hydrogen separation process to thereby generate hydrogen and a hydrogen-depleted shifted gas; and

performing a carbon dioxide separation process on the hydrogen-depleted shifted gas to thereby generate carbon dioxide;

wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

outputting hydrogen from the permeate side of the Palladium membrane; and

outputting hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

2. The method according to clause 1, further comprising performing a sulfur removal process on the feed gas before performing the reforming processes on the feed gas.

3. The method according to clause 1 or 2, further comprising performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; and

the method further comprising:

optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and

optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

4. The method according to any of the preceding clauses, wherein the carbon dioxide separation process generates carbon dioxide and a rest gas, and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one of said performed processes in the method of producing hydrogen.
5. The method according to clause 4, wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.
6. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the autothermal reforming process.
7. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the water-gas-shift process.
8. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
9. The method according to any of the preceding clauses, wherein the feed gas is natural gas.
10. The method according to any of the preceding clauses, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
11. The method according to any of the preceding clauses, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

12. The method according to any of the preceding clauses, wherein the autothermal reforming process is supplied with oxygen from an air separation unit.

5 13. The method according to any preceding clause, wherein the water-gas-shift process is conducted in one water-gas-shift reactor.

14. The method according to clause 13, wherein the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably  
10 between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C.

15. The method according to any of the preceding clauses, wherein the water-gas-shift process and the hydrogen separation process are operated at about  
15 the same temperature.

16. The method according to any of the preceding clauses, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

20 17. The method according to any of the preceding clauses, wherein the water-gas-shift process comprises using a Cu-based catalyst.

18. The method according to any of the preceding clauses, further comprising  
25 operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

19. The method according to any of the preceding clauses, wherein water is separated from the hydrogen-depleted shifted gas output from the hydrogen  
30 separation process.

20. The method according to any of the preceding clauses, wherein water is not separated from the shifted gas before the hydrogen separation process.

21. The method according to any of the preceding clauses, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

5 22. The method according to any of the preceding clauses, wherein the carbon dioxide separation process is conducted cryogenically.

23. The method according to clause 12, or any clause dependent thereon, wherein the air separation unit is also arranged to generate nitrogen, and the  
10 method comprises generating ammonia in dependence on nitrogen output from the air separation unit and hydrogen output from the hydrogen separation process.

24. A hydrogen production plant arranged to perform the method of any of clauses  
15 1 to 22.

25. An ammonia production plant arranged to perform the method of clause 23.

The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather,  
20 the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without departing from the spirit and scope of the invention as set forth  
25 in the appended claims.

From the INTERNATIONAL BUREAU

**PCT****NOTIFICATION OF THE RECORDING  
OF A CHANGE**(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

J A KEMP LLP  
80 Turnmill Street  
London EC1M 5QU  
ROYAUME-UNI

|                                                                    |                                                                             |
|--------------------------------------------------------------------|-----------------------------------------------------------------------------|
| Date of mailing (day/month/year)<br>30 September 2021 (30.09.2021) | <b>IMPORTANT NOTIFICATION</b>                                               |
| Applicant's or agent's file reference<br>N418823WO HHG             |                                                                             |
| International application No.<br>PCT/EP2021/054441                 | International filing date (day/month/year)<br>23 February 2021 (23.02.2021) |

1. The following indications appeared on record concerning:

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

|                                                                                                                       |                                   |                    |
|-----------------------------------------------------------------------------------------------------------------------|-----------------------------------|--------------------|
| Name and Address<br>J A KEMP LLP<br>14 South Square<br>Gray's Inn<br>London Greater London WC1R 5JJ<br>UNITED KINGDOM | State of Nationality              | State of Residence |
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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<br>J A KEMP LLP<br>80 Turnmill Street<br>London EC1M 5QU<br>UNITED KINGDOM | State of Nationality                                                                                        | State of Residence |
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|                                                                                             | Facsimile No.                                                                                               |                    |
|                                                                                             | E-mail address<br>mail@jakemp.com<br><input checked="" type="checkbox"/> 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 Preliminary Examining Authority  
☐ the International Searching Authority ☒ the designated Offices concerned  
☐ the Authority(ies) specified for supplementary search ☐ the elected Offices concerned  
☐ other:

|                                                                                               |                                                                                                          |
|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| The International Bureau of WIPO<br>34, chemin des Colombettes<br>1211 Geneva 20, Switzerland | Authorized officer<br><br>Blanc Veronique<br>e-mail pct.team5@wipo.int<br>Telephone No. +41 22 338 74 05 |
|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|

**PCT REQUEST**

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|              |                                                                                                                                                |                                                                         |
|--------------|------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| <b>0</b>     | <b>For receiving Office use only</b>                                                                                                           |                                                                         |
| <b>0-1</b>   | International Application No.                                                                                                                  | <b>PCT/EP2021/054441</b>                                                |
| <b>0-2</b>   | International Filing Date                                                                                                                      | <b>23 FEB 2021 (23.02.2021)</b>                                         |
| <b>0-3</b>   | Name of receiving Office and "PCT International Application"                                                                                   | <b>RO/EP</b>                                                            |
| <b>0-4</b>   | <b>Form PCT/RO/101 PCT Request</b>                                                                                                             |                                                                         |
| <b>0-4-1</b> | Prepared Using                                                                                                                                 | PCT Online Filing<br>Version 3.51.000.269e MT/FOP<br>20141031/0.20.5.24 |
| <b>0-5</b>   | <b>Petition</b><br>The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty |                                                                         |
| <b>0-6</b>   | <b>Receiving Office (specified by the applicant)</b>                                                                                           | <b>European Patent Office (EPO) (RO/EP)</b>                             |
| <b>0-7</b>   | <b>Applicant's or agent's file reference</b>                                                                                                   | <b>N418823WO HHG</b>                                                    |
| <b>I</b>     | <b>Title of Invention</b>                                                                                                                      | <b>HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS</b>                       |
| <b>II</b>    | <b>Applicant</b>                                                                                                                               |                                                                         |
| II-1         | This person is                                                                                                                                 | Applicant only                                                          |
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|              |                                  |                                               |
|--------------|----------------------------------|-----------------------------------------------|
| <b>III-3</b> | <b>Applicant and/or inventor</b> |                                               |
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| III-6-3      | Inventor for                     | All designated States                         |
| III-6-4      | Name (LAST, First)               | OSTADI, Mohammad                              |
| III-6-5      | Address                          | Vegamot 1 O<br>7049 Trondheim 107<br>Norway   |



## PCT REQUEST

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|                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                         |
|----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|
| <b>IV-1</b>    | <b>Agent or common representative; or address for correspondence</b><br>The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | <b>Agent</b>                                                                            |
| IV-1-1         | Name                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | J A Kemp LLP                                                                            |
| IV-1-2         | Address                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 14 South Square<br>Gray's Inn<br>London<br>Greater London<br>WC1R 5JJ<br>United Kingdom |
| IV-1-3         | Telephone No.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | +44 20 3077 8600                                                                        |
| IV-1-5         | e-mail                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | mail@jakemp.com                                                                         |
| IV-1-5(a)<br>) | E-mail authorization<br>The receiving Office, the International Searching Authority, the International Bureau and the International Preliminary Examining Authority are authorized to use this e-mail address, if the Office or Authority so wishes, to send notifications issued in respect of this international application:                                                                                                                                                                                                                                                                                                                                                                                                                   | exclusively in electronic form (no paper notifications will be sent)                    |
| <b>V</b>       | <b>DESIGNATIONS</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                         |
| <b>V-1</b>     | 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.                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                         |
| <b>VI-1</b>    | <b>Priority claim of earlier national application</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                         |
| VI-1-1         | Filing date                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 06 March 2020 (06.03.2020)                                                              |
| VI-1-2         | Number                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 2003317.1                                                                               |
| VI-1-3         | Country or Member of WTO                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | GB                                                                                      |
| <b>VI-2</b>    | <b>Priority claim of earlier national application</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                         |
| VI-2-1         | Filing date                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 02 July 2020 (02.07.2020)                                                               |
| VI-2-2         | Number                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 2010174.7                                                                               |
| VI-2-3         | Country or Member of WTO                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | GB                                                                                      |
| <b>VI-3</b>    | <b>Priority document request</b><br>The International Bureau is requested to obtain from a digital library a certified copy of the earlier application(s) identified above as item(s), using, where applicable, the access code(s) indicated:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | VI-1 Access code: 8A1E<br>VI-2 Access code: C3D0                                        |
| <b>VI-4</b>    | <b>Incorporation by reference :</b><br>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), or an element or part of the description, claims or drawings referred to in Rule 20.5bis(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. |                                                                                         |
| <b>VII-1</b>   | <b>International Searching Authority Chosen</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | European Patent Office (EPO) (ISA/EP)                                                   |

**PCT REQUEST**

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|             |                                                                                                                                      |                                                                                                                                                                                                         |                                    |
|-------------|--------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|
| <b>VIII</b> | <b>Declarations</b>                                                                                                                  | <b>Number of declarations</b>                                                                                                                                                                           |                                    |
| 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                                                       | —                                                                                                                                                                                                       |                                    |
| <b>IX</b>   | <b>Check list</b>                                                                                                                    | <b>Number of sheets</b>                                                                                                                                                                                 | <b>Electronic file(s) attached</b> |
| IX-1        | Request (including declaration sheets)                                                                                               | 5                                                                                                                                                                                                       | ✓                                  |
| IX-2        | Description                                                                                                                          | 33                                                                                                                                                                                                      | ✓                                  |
| IX-3        | Claims                                                                                                                               | 5                                                                                                                                                                                                       | ✓                                  |
| IX-4        | Abstract                                                                                                                             | 1                                                                                                                                                                                                       | ✓                                  |
| IX-5        | Drawings                                                                                                                             | 16                                                                                                                                                                                                      | ✓                                  |
| IX-6a       | Sequence listing part of the description (also to be used for the purposes of international search)                                  | —                                                                                                                                                                                                       | —                                  |
| IX-7        | TOTAL                                                                                                                                | 60                                                                                                                                                                                                      |                                    |
|             | <b>Accompanying Items</b>                                                                                                            | <b>Paper document(s) attached</b>                                                                                                                                                                       | <b>Electronic file(s) attached</b> |
| IX-8        | Fee calculation sheet                                                                                                                | —                                                                                                                                                                                                       | ✓                                  |
| IX-19       | Other                                                                                                                                | Pre-conversion archive Statement (Section 706): This is a complete and accurate copy of the international application prior to its conversion into the electronic document format in which it is filed. | ✓                                  |
| IX-20       | Figure of the drawings which should accompany the abstract                                                                           | 9                                                                                                                                                                                                       |                                    |
| 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                                                                                                                                 | J A Kemp LLP                                                                                                                                                                                            |                                    |
| X-1-2       | Name of signatory                                                                                                                    | Henry Hunt-Grubbe 33527                                                                                                                                                                                 |                                    |
| X-1-3       | Capacity (if such capacity is not obvious from reading the request)                                                                  | (Representative)                                                                                                                                                                                        |                                    |

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| 10-1   | Date of actual receipt of the purported international application                                                                       | 23 FEB 2021 (23.02.2021) |
| 10-2   | Drawings:                                                                                                                               | Received                 |
| 10-2-1 | Received                                                                                                                                |                          |
| 10-2-2 | Not received                                                                                                                            |                          |
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| 10-4   | Date of timely receipt of the required corrections under PCT Article 11(2)                                                              |                          |
| 10-5   | International Searching Authority                                                                                                       | ISA/EP                   |
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*C01B 3/48* (2006.01) *C01B 3/50* (2006.01)

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**(54) Title:** HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

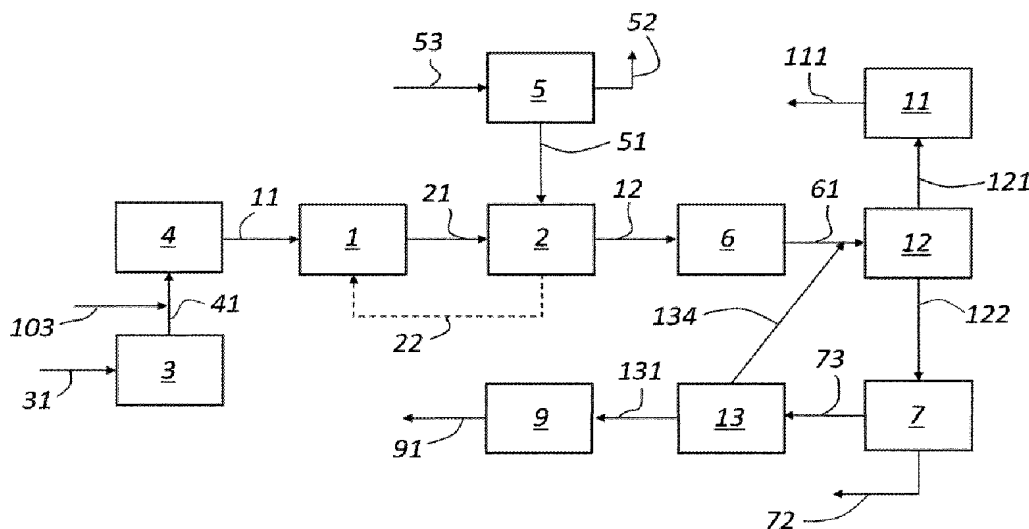


FIGURE 9

**(57) Abstract:** Disclosed herein is a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the one or more reforming processes, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process; wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.

NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW,  
SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN,  
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- with international search report (Art. 21(3))
- with amended claims (Art. 19(1))

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Newport  
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Patents Act 1977 (Rule 12)

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Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

Application number GB 2010174.7

|                                                                                                                                                                                                                                                   |                                                                                                                                   |                                      |                                     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|-------------------------------------|
| 1. Your reference                                                                                                                                                                                                                                 | <b>N418823GB-A HHG</b>                                                                                                            |                                      |                                     |
| 2. Full name, address and postcode of the applicant or of each applicant                                                                                                                                                                          | <b>Reinertsen New Energy AS<br/>Leiv Eiriksson Senter<br/>Trondheim 7010<br/>Norway</b>                                           |                                      |                                     |
| Patents ADP number (if you know it)                                                                                                                                                                                                               |                                                                                                                                   |                                      |                                     |
| 3. Title of the invention                                                                                                                                                                                                                         | <b>HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS</b>                                                                                 |                                      |                                     |
| 4. Name of your agent (if you have one)<br>"Address for service" to which all correspondence should be sent. This may be in the European Economic area or Channel Islands (see warning note below)<br>(including the postcode)                    | <b>J A Kemp LLP<br/>J A Kemp LLP<br/>14 South Square<br/>Gray's Inn<br/>London WC1R 5JJ<br/>Greater London<br/>United Kingdom</b> |                                      |                                     |
| Patents ADP number (if you know it)                                                                                                                                                                                                               |                                                                                                                                   |                                      |                                     |
| 5. Priority declaration: Are you claiming priority from one or more earlier-filed patent applications? If so, please give details of the application(s)                                                                                           |                                                                                                                                   |                                      |                                     |
| Country<br><b>United Kingdom</b>                                                                                                                                                                                                                  | Application number<br><b>2003317.1</b>                                                                                            | Date of filing<br><b>06 Mar 2020</b> | PDAS Access Code<br><b>8A1E</b>     |
| 6. Divisionals etc: Is this application a divisional application, or being made following resolution of an entitlement dispute about an earlier application. If so, please give the application number and filing date of the earlier application |                                                                                                                                   | Number of earlier UK application     | Date of filing (day / month / year) |
| 7. Inventorship: (Inventors must be individuals not companies)                                                                                                                                                                                    |                                                                                                                                   |                                      |                                     |
| Are all the applicants named above also inventors?                                                                                                                                                                                                |                                                                                                                                   | <b>No</b>                            |                                     |
| 8. Are you paying the application fee with this form?                                                                                                                                                                                             |                                                                                                                                   | <b>Yes</b>                           |                                     |



## Patents Form 1

9. Accompanying documents: please enter the number of pages of each item accompanying this form.

Continuation sheets of this form

Description: **33**

Claim(s): **5**

Abstract: **1**

Drawing(s): **16**

If you are not filing a description, please give details of the previous application you are going to rely upon

| Country                                                                            | Application number | Date of filing | PDAS Access Code |
|------------------------------------------------------------------------------------|--------------------|----------------|------------------|
| 10. If you are also filing any of the following, state how many against each item. |                    |                |                  |

Priority documents: **0**

Statement of inventorship and right to grant of a patent  
(Patents Form 7): **1**

Request for search (Patents Form 9A): **1**

Request for a substantive examination (Patents Form 10): **1**

Any other documents (please specify): **Pre-conversion Archive  
PDAS Registration Form  
PDAS Request Form**

11. I/We request the grant of a patent on the basis of this application.

Signature: **Subject: Henry Hunt-Grubbe 33527; Issuer:** Date: **02 Jul 2020**  
**European Patent Office, European Patent  
Office CA G2**

12. Name, e-mail address, telephone, fax and/or mobile number, if any, of a contact point for the applicant
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## HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### FIELD

The present disclosure relates to hydrogen and ammonia production processes. Embodiments provide a system for generating syngas and then separating hydrogen from the syngas. The system according to embodiments may use the separated hydrogen to generate ammonia.

### BACKGROUND

It is generally believed that the greenhouse effect and the climate on Earth are closely linked to human-made emissions of carbon dioxide (CO<sub>2</sub>). These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines. A desirable goal is to reduce the emission of CO<sub>2</sub> to the atmosphere. It is known art to reduce the emission of CO<sub>2</sub> from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen and carbon dioxide. These components are then separated, after which hydrogen may be used in a number of applications, such as electricity generation, heat generation and in different types of transportation. Hydrogen may also be mixed with natural gas to produce hytane, a fuel a fuel for domestic and industrial energy users. Carbon dioxide has industrial applications but may also be deposited after compression to a desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.

Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen that is made by splitting water through electrolysis and compressed to typically 700 bar. Liquid hydrogen is being considered for heavier transport like ships and trains. Unfortunately, electrolysis has been calculated to be at least twice as costly as producing hydrogen by reforming natural gas. These calculations include costs of separation and liquefaction of coproduced CO<sub>2</sub> and

payment of tariffs for deposition of CO<sub>2</sub> in underground reservoirs. Another complicated issue with water electrolysis is calculation of the greenhouse effect, as most electricity is still produced from hydrocarbons with significant emission of CO<sub>2</sub> to the atmosphere. Therefore, producing hydrogen from natural gas with CO<sub>2</sub> storage is a significantly better option.

There is a general need to improve hydrogen production processes.

## SUMMARY OF INVENTION

According to a first aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; performing a reforming process on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the reforming process, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process; wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.

Preferably, the reforming process comprises an autothermal reforming process.

Preferably, the reforming process comprises a gas heated reforming process.

Preferably, the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

Preferably, the method further comprises: optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; wherein the pre-reforming process comprises: optionally saturating the feed gas with at least water before performing

the pre-reforming processes on the feed gas; and optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

Preferably, the hydrogen separation process comprises: inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen  
5 separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane; outputting hydrogen from the permeate side of the Palladium membrane; and outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

10 Preferably, the hydrogen separation process comprises a PSA process.

Preferably, the rest gas that is recycled is fed back into the autothermal reforming process.

Preferably, the rest gas that is recycled is fed back into the water-gas-shift process.

Preferably, the rest gas that is recycled is fed back into the hydrogen separation  
15 process.

Preferably, the feed gas is natural gas.

Preferably, the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.

Preferably, the temperature of the gas exiting the gas-heated reforming process is in  
20 the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

Preferably, the autothermal reforming process is supplied with oxygen from an air separation unit.

Preferably, the water-gas-shift process is conducted in one water-gas-shift reactor; wherein, optionally, the water-gas shift reactor is operated at a temperature between  
25 about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C; and wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

Preferably, the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

Preferably, no additional steam is added between the reforming processes and the water-gas-shift process.

- 5 Preferably, the method further comprises operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

Preferably, water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

- 10 Preferably, water is not separated from the shifted gas before the hydrogen separation process.

Preferably, the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

- 15 Preferably, the carbon dioxide separation process is conducted cryogenically.

Preferably, the method further comprises generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

- 20 According to second aspect of the present invention, there is provided a hydrogen production plant arranged to perform the method of the first aspect.

According to third aspect of the present invention, there is provided an ammonia production plant arranged to perform the method of the first aspect.

## **BRIEF DESCRIPTION OF DRAWINGS**

- 25 Figure 1 shows a reforming process comprising a gas-heated reforming process and an autothermal reforming process.

Figure 2 shows a configuration of a hydrogen production process.

Figure 3 shows a configuration of a hydrogen production process according to an embodiment.

Figure 4 shows a configuration of a hydrogen production process according to an embodiment.

- 5 Figure 5 shows a configuration of a hydrogen production process according to an embodiment.

Figure 6 shows a configuration of a hydrogen production process according to an embodiment.

- 10 Figure 7 shows a configuration of a hydrogen production process according to an embodiment.

Figure 8 shows a configuration of a hydrogen production process according to an embodiment.

Figure 9 shows a configuration of a hydrogen production process according to an embodiment.

- 15 Figure 10 comprises Table 1.

Figure 11 comprises Table 2.

Figure 12 comprises Table 3.

Figure 13 comprises Table 4.

Figure 14 comprises Table 5.

- 20 Figure 15 comprises Table 6.

Figure 16 shows a configuration of an ammonia production process according to an embodiment.

## **DETAILED DESCRIPTION OF EMBODIMENTS**

- 25 A known method for the production of a CO<sub>2</sub>-rich gas stream and a H<sub>2</sub>-rich gas stream comprises the following steps:

a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas, also referred to as syngas, under supply of an O<sub>2</sub>-containing gas. Syngas mainly comprises H<sub>2</sub> and CO;

b) the gas stream from a) is shifted so as to produce a mixture of H<sub>2</sub> and CO<sub>2</sub> by reaction with H<sub>2</sub>O;

c) CO<sub>2</sub> is separated from the gas stream from b) in a CO<sub>2</sub> separation unit;

d) H<sub>2</sub> is separated from the CO<sub>2</sub>-depleted gas from c) in a H<sub>2</sub> separation unit.

The above method describes the basic principles behind the production hydrogen from natural gas with separation of hydrogen and CO<sub>2</sub>.

Known techniques combust the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> as fuel. If a relatively high percentage of hydrogen has not been separated, then a significant amount of hydrogen will be wasted in this fuel. Furthermore, the combustion of any accompanying carbon containing species in the fuel produces uncaptured CO<sub>2</sub>.

Most hydrogen producing processes from natural gas known in the art rely on the use of a steam reformer, and in some instances on an autothermal reformer (ATR), i.e. using an autothermal reactor, or a partial oxidation reactor. However, use of a gas-heated-reformer (GHR) in combination with an autothermal reformer is considerably more energy efficient.

Production and perspectives on syngas production has been described by J. R. Rostrup-Nielsen in *Catalysis Today*, volume 18, pages 305-324, 1993, and in volume 71, pages 243-247, 2002. There are several types of reformers for production of synthesis gas comprising steam reforming, autothermal reforming and partial oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.

Separation of CO<sub>2</sub> is frequently done by an amine washing process, and sometimes by using a physical sorbent like methanol.

Hydrogen may be separated from a hydrogen containing gas mixture by use of a pressure swing absorption/adsorption (PSA) processor. In some implementations of PSA processes by a PSA reactor, the PSA reactor is a large and costly part of the hydrogen plant. PSA processes may also result in CO<sub>2</sub> being released at low pressure, e.g. atmospheric pressure, and so there is a subsequent need for compression and cooling.

Embodiments provide new and particularly advantageous implementations of systems for producing hydrogen from natural gas. Hydrogen production may be the main purpose of the system. However, embodiments also include using at least some of the hydrogen to produce ammonia. Ammonia is an alternative energy carrier to compressed or liquefied hydrogen. In addition to the production of fertilizers, ammonia may be used as fuel in transportation, maritime and offshore markets.

Embodiments also provide a high carbon capture efficiency that may be at least 90% of the carbon in the feed gas, and preferably at least 97%.

Although embodiments may separate CO<sub>2</sub> by using an amine washing process, or other process, embodiments preferably use cryogenic separation to separate CO<sub>2</sub>. That is to say, the gas stream is cooled to a temperature, and at a pressure, where CO<sub>2</sub> is liquefied.

Cryogenic separation of CO<sub>2</sub> has in the known art been assumed to be disadvantageous as a smaller fraction of CO<sub>2</sub> is separated. However, embodiments avoid this disadvantage by providing novel process design. CO<sub>2</sub> is obtained directly in a liquid form, i.e. ready for transportation to a deposition site.

Embodiments advantageously re-use the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> in the hydrogen production system. This improves the carbon capture efficiency of the system.

Embodiments include using a Palladium membrane (Pd-membrane) to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons. One advantage is that hydrogen is obtained with high purity; that may be greater than 99% and is often greater than 99.9%. Another advantage is that the gas containing CO<sub>2</sub> that does not pass through the membrane,



which is referred to as the retentate, is at an elevated pressure, typically above 10 bar, more typically between 20 and 40 bar, but sometimes even at pressures up to 80 bar. It is even preferred that the Pd-membrane operates at an elevated temperature; 200-400 °C, or in a narrower range above or around 300 °C, so that it is well suited for operation down-stream of the water-gas-shift (WGS) reactor or reactors.

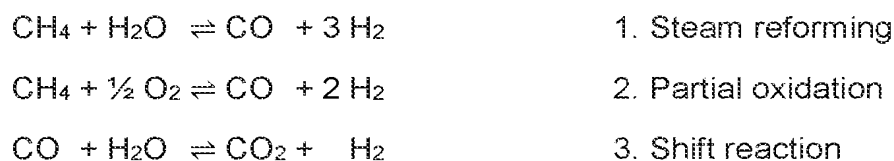
Embodiments also include using a PSA process, or PSA processes, to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons.

Embodiments include receiving a supply of natural gas, or more generally a hydrocarbon containing gas from any source. The natural gas may be cleaned and pre-treated in a suitable manner so that the gas feed mainly comprises methane after treatment. Such cleaning typically comprises sulfur removal, for example by an ZnO absorber. The pre-treatment may also comprise a pre-reforming process whereby higher hydrocarbons, such as ethane, are converted by steam to methane and CO<sub>2</sub>.

The reforming process according to embodiments may take place at a pressure within the interval 10 to 200 bar.

The water-gas shift reaction according to embodiments may take place in a shift reactor. Steam may be supplied to the shift reactor, but the shift reactor may also be operated without supply of steam as steam already is introduced into the reformer. At the outlet of the shift reactor, the carbon content may comprise CO<sub>2</sub> and methane. CO<sub>2</sub> may be about 2% to about 5% by volume or higher. Methane may be about 2% to about 5% by volume or higher.

The following chemical reactions may take place during production of synthesis gas and hydrogen by reforming of natural gas:



The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by partial oxidation in an autothermal reformer.

In a steam reformer (SR) natural gas (i.e. methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer consists of many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer is approximately 950 °C. The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the produced stream is from 2.7 to 3.0. Synthesis gas produced from a steam reformer may contain approximately 3% methane by volume.

Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR, natural gas (methane) is fed together with oxygen or air into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions may be driven to equilibrium over a catalyst bed before the synthesis gas leaves the reactor at approximately 1000-1050 °C. The size of such a unit could be a height of 10-15 meters and a diameter of 5-6 meters. A typical ratio of steam:carbon in the output gas is from 0.6 to 1.4. The ratio of hydrogen to carbon monoxide in the output gas is lower than 2. Typical methane slip, i.e. amount of unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR.

A further option for reforming natural gas is a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed. The exit temperature for a POX is somewhat higher than for a typical ATR.

Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. In combined reforming, SR is operated at milder conditions (i.e. lower outlet temperature), which leads to a high methane slip. The residual methane is then reacted in the ATR. The ratio of steam:carbon is in the area 1.8-2.4, with a ratio of hydrogen to carbon monoxide in the product gas higher than 2.

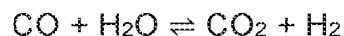
From the above, it is clear that the reformer unit has a very large footprint (SR), and that the exit gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB) that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting. It has been found, however, that a more efficient process is experienced if the hot output gas is used to reform part of the natural gas before it enters the autothermal reformer. This combination of ATR with oxygen and a gas-heated-reformer (GHR) has been tested in a demonstration unit for production of methanol. This development originates in ICI in the 1980s to completely remove the traditional steam reformer in their Leading Concept Methanol (LCM) process.

Figure 1 shows an efficient reforming process that may be used in embodiments. The hot exit gas from the reformer is used to reform part of the natural gas before it enters the autothermal reformer. Instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR 1, then the partially reformed gas in stream 21 passes through the ATR 2, and finally the reformed gas in stream 22 passes through the heating side of the GHR 1 to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only moderate further cooling before the water-gas-shift process (WGS).

Although embodiments include the reforming process shown in Figure 1, embodiments also include alternatively using any other type of reforming process.

For example, embodiments include only using an autothermal reformer or only using a gas-heated-reformer.

After reforming of the natural gas and cooling, the gas mixture is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and some CH<sub>4</sub>. Between these components there is an equilibrium relation given by the stoichiometric equation:



This reaction is called the water-gas-shift (WGS) reaction, and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors may be used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used.

Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. The catalyst in the first step may be based on chromium/iron, whereas the catalyst in the second step may be a copper/zinc catalyst. In the shift unit CO and H<sub>2</sub>O are reacted to form CO<sub>2</sub> and H<sub>2</sub>, and in known techniques it is often a requirement that the mentioned reaction is driven to the right to the highest possible degree, so that as little CO as possible is present in the gas mixture exiting the shift unit. A low content of CO in the mentioned gas mixture again gives a high purity of the H<sub>2</sub>-rich gas stream out of the separation unit.

In known techniques the shift reactor is operated so that the ratio H<sub>2</sub>O:CO to the shift reactor is high, e.g. equal to 10:1, so that there is a high conversion of CO.

Embodiments may differ from such techniques by optimizing the processes in a WGS reactor in conjunction with a hydrogen separation processes by a Palladium membrane. The efficiency of a Pd membrane may be improved by operating at a certain elevated temperature. Preferably, only a high-temperature WGS is therefore applied before the membrane. A low-temperature WGS may also be used after the membrane and the shifted gas partly recycled, i.e. fed back into one of the earlier processes in the hydrogen production process.

In a preferred embodiment, the temperature of the WGS process is determined in dependence on an operating condition of the Pd-membrane. For example, the temperature of the WGS process may be set substantially at the operating condition of the Pd-membrane, e.g. about 300 °C, thereby avoiding any need for heat exchange between the two units. It is not necessary for the WGS process to be operated in a way that maximizes the conversion of CO because the rest gas is recycled back into the earlier processes. Embodiments include no additional steam being added before the WGS reactor. When the Pd-membrane is operated at about 300 °C, a Cu-based catalyst may be used.

Gases in the mixture after the shift reactor, or the shift reactors, can be separated more or less completely based on the different properties of the gas molecules. The most common techniques are absorption, adsorption and cryogenic distillation.

CO<sub>2</sub> is an acid gas, and the most widely used method to separate the mentioned gas from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by altering the composition of the liquid or by altering pressure and temperature. For separation of CO<sub>2</sub>, aqueous solutions of alcoholamines can be used. The absorption takes place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO<sub>2</sub> from the amine phase in the stripping unit, stripping steam is usually used. If the partial pressure of CO<sub>2</sub> in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO<sub>2</sub> can be set free in the stripping unit at elevated pressure,

e.g. 5-8 bar. Other absorption technologies rely on alternative physical liquid absorbents like methanol at reduced temperature.

Embodiments preferably separate hydrogen from the gas output from the WGS reactor using a membrane. In particular, a Pd-film membrane may be used. By the use of one or more semipermeable or dense membrane units, molecules of different size and different properties can be made to permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture from the WGS reactor, membranes can be selected where  $H_2$  permeates rapidly, whereas  $CO_2$  permeates slowly or not at all, so that separation of the different gas components is achieved. The membrane may be a Palladium membrane.

The driving force over the membrane is the difference in partial pressure, i.e. of hydrogen between the process gas (which is the received gas on the retentate side of the membrane) and gas on the permeate side of the membrane. As hydrogen in many cases is required at an elevated pressure, a way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. Although embodiments include using a sweep gas, this is optional and embodiments also include not using a sweep gas.

Embodiments may alternatively use a combination of solid membranes and liquid membranes through which there is a rapid permeation of  $CO_2$ , while  $H_2$  is kept back.

Embodiments may alternatively use PSA to separate hydrogen from the gas output from the WGS reactor. PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material. In the present mixture of gases,  $CO$ ,  $CO_2$  and  $CH_4$  are adsorbed, letting the hydrogen pass through at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit. Alternatively, the temperature can swing instead of the pressure.

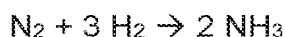
Capturing CO<sub>2</sub> by refrigeration is a cost and energy efficient method compared to other technologies. In known techniques, electricity may be used to drive the compressors. The main challenge has been that only in the order of 90% of CO<sub>2</sub> is captured this way, or perhaps 93% by optimizing conditions. In addition, there are  
5 some carbon losses from unconverted CO and CH<sub>4</sub> and these reduce the overall carbon capture to 90% or below.

Embodiments include separating out CO<sub>2</sub> and then depositing the separated CO<sub>2</sub>. Large amounts of CO<sub>2</sub> can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water reservoirs and deposition in  
10 oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO<sub>2</sub> gas has to be brought to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO<sub>2</sub> gas  
15 can be separated from the H<sub>2</sub>/CO<sub>2</sub> mixture at an elevated pressure, significant compression work can be avoided.

Embodiments may allow a selection to be made between collecting hydrogen and CO<sub>2</sub> at the high (process) pressure. A hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen, is needed for storage and in  
20 transportation applications. As it is more demanding to pressurize hydrogen than CO<sub>2</sub>, separation technologies that provide hydrogen at high pressure are sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen-permeable membrane.

Embodiments include using an air separation unit (ASU) to generate oxygen. The  
25 oxygen may be supplied to an autothermal reactor, ATR, used in the reforming process. The ASU may cryogenically separate air into oxygen and a gas mixture that mostly comprises nitrogen. Embodiments include using the nitrogen, from the ASU, and hydrogen, from the membrane separator, to generate ammonia.

Combining nitrogen with hydrogen allows production of ammonia, NH<sub>3</sub>, according to  
30 the reaction:



Ammonia can be used as an environmentally friendly fuel as long as any CO<sub>2</sub> generated during production is captured. The benefits of using ammonia include ease of transportation and handling. Liquid ammonia can be stored in vessels at about 17 bar.

The ammonia process is favored by high pressures, and an elevated temperature is needed for sufficient reaction rate.

A known production technique of ammonia is from natural gas, or sometimes from higher hydrocarbons, by reforming the gas to syngas that is shifted to mostly hydrogen and CO<sub>2</sub>. Using air in the process stream, like applying an ASU, gives a mixture of hydrogen, nitrogen, water and CO<sub>2</sub> after shift conversion. The shift reaction is frequently carried out in two steps, high-temperature and low-temperature shift, to convert CO to low levels. Before the ammonia synthesis, water is knocked out and CO<sub>2</sub> removed by elaborate means. Further, residual CO and CO<sub>2</sub> has to be removed as they are poisons for the catalyst, and this is done by methanation;



The ammonia synthesis loop is also known as Haber-Bosch synthesis. The reaction is run over a catalyst that typically is promoted magnetite. Single pass conversion over the catalyst is around or below 20% and, therefore, significant recycle is required. The pressure is in the range 60-200 bar depending on process design. This is significantly higher than reforming and shifting natural gas that takes place in the pressure range 20-35 bar. On the other hand, the reaction pressure to make ammonia is significantly lower than the 300-700 bar required for hydrogen as energy carrier. Reaction temperature is ca. 450 °C. There have been many types of design of ammonia plants during the last 60 years. One option that has been explored is to produce hydrogen from steam reforming combined with PSA, and combined this hydrogen with nitrogen from an ASU-unit. Such a plant, however, is not favorably designed for separating a pure CO<sub>2</sub>-stream for storage.



Embodiments are described in more detail by the following examples of embodiments and figures.

Process simulations using the program UniSim are based on natural gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher

- 5 hydrocarbons, 1.5% CO<sub>2</sub> and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. The natural gas flow is 4625 kg/h; 246 kmol/h. Hydrogen specification is > 99.97 mol% for fuel cells, and specification for CO<sub>2</sub> is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C.

- 10 A number of process schemes are analyzed. These include one comparative example and a number of implementations of embodiments, four of which are summarized in Table 1 in Figure 10. The schemes vary in WGS temperature, use of Pd-membrane or PSA for hydrogen separation, use of amine solvents or cryogenic CO<sub>2</sub> separation, as well as the position of water condensation.

- 15 The membrane may be always operated at a preferable temperature for permeation of hydrogen through the membrane. For example, the membrane may be operated at 300 °C. However, the WGS may be operated at 256 °C for highest CO conversion, but at 300 °C when the shifted gas is directly introduced to the membrane; i.e. without any heat exchange and water condensation.

- 20 The conditions of Embodiment Example 2 are applied in Embodiment Examples 5-7, where recycle of rest gas is used.

- 25 The following reasonable assumptions are made, but without fixing these conditions: in amine cases, it is assumed that 100% of inlet CO<sub>2</sub> is removed by the unit; in membrane cases, 93% H<sub>2</sub> separation is assumed; produced H<sub>2</sub> from the membrane unit is at 3 bar and compressed to 350 bar for export; the final CO<sub>2</sub> stream is delivered at -26.2 °C at 16 bar. It is understood that the applied conditions are reasonable for comparing different process schemes, but that a variety of other conditions can be used; e.g. for different natural gas compositions, requirements for delivery of hydrogen and CO<sub>2</sub>, and site specific conditions like possibilities for integration with other process units and the availability of electricity from the grid.

- 30 **Comparative Example**

Figure 2 is a process flow sheet showing production of hydrogen and CO<sub>2</sub> by combination of ATR 2 and GHR 1 according to a comparative example to embodiments.

The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen stream 101 is optionally added to the pretreated natural gas 41 as stream 103 and fed to the optional pre-reformer 4. The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen 51 from an air separation unit (ASU) 5 is added to the ATR 2. The ASU separates cryogenically air 53 into oxygen 51 and nitrogen 52, sometimes also producing noble gases like argon. It should be understood that embodiments include any other means for producing oxygen, or air enriched in oxygen, such as by using vacuum or pressure swing adsorption, or by using a membrane.

The produced syngas 12 is shifted to increase the content of hydrogen and CO<sub>2</sub> in one or more shift reactors 6, i.e. water-gas-shift reactor(s) 6, to produce the shifted gas 61. Steam may be added to the gas mixture before the gas mixture is input into the shift reactor(s) 6. The addition of steam increases the efficiency of the shift reaction. The shifted gas 61 is subsequently cooled in the condenser 7 to remove its water content 72, thus obtaining dry shifted syngas 71. Amine type separation process 8 separates CO<sub>2</sub> 81 from the shifted gas, and the CO<sub>2</sub> 81 is then compressed 9 and liquefied. The produced CO<sub>2</sub> 91 may be stored at site, shipped for permanent storage or directly injected into a geological formation for storage.

Hydrogen 101 is separated in the process 10 by the known technique of pressure-swing absorption/adsorption (PSA), that separates the hydrogen from the gas 82 that has already been depleted of CO<sub>2</sub> by the process 8. The separate outputs from the process 10 are hydrogen 101 and a rest gas 102. The rest gas 102 contains remnants of CO and CH<sub>4</sub> together with unseparated CO<sub>2</sub> and hydrogen. The energy in the rest gas is utilized for fuel in fired heater(s) for preheating of feed gases natural gas and water/steam. Finally, the produced hydrogen 101 is compressed 11 to give hydrogen 111 at 340 bar.

The simulations show that production of 100 kNm<sup>3</sup>/hr hydrogen requires 35.7 kNm<sup>3</sup>/hr of NG and 16.7 kNm<sup>3</sup>/hr of oxygen. 622 tons of CO<sub>2</sub> is captured each year, assuming that the PSA rest gas 102 is used for combustion and the exhaust gas CO<sub>2</sub> emitted to the atmosphere. This gives a CO<sub>2</sub> capture efficiency of 95.4%. Electric power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

### Embodiment example 1

Figure 3 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 1. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

The present embodiment differs from the above-provided comparative example in that hydrogen separation is performed before CO<sub>2</sub> separation. After the WGS process, the shifted gas enters a hydrogen separation vessel that comprises a Pd-membrane 12. The hydrogen separation vessel may receive the output gas from the WGS reactor on the retentate side of the Pd-membrane. Hydrogen passes through the Pd-membrane to reach a permeate side of the Pd-membrane. The hydrogen on the permeate side of the Pd-membrane is output as stream 121. The gas stream output from the retentate side of the Pd-membrane is hydrogen-depleted gas 122.

The hydrogen stream 121 is sent to compressor 11 while the hydrogen-depleted gas stream 122 is depleted of water 72 in the condenser 7. The dried gas 73 is then input into the amine separator 8 that outputs CO<sub>2</sub> stream 81 and a rest gas 83. CO<sub>2</sub> stream 81 is compressed 9, and the CO<sub>2</sub> depleted rest gas 83 may be used for providing energy in fired heater(s).

Advantageously, the use of a Pd-membrane separator for separating hydrogen as the subsequent process to the WGS process allows the hydrogen separation process to be performed particularly efficiently and effectively. In particular, the temperature

and/or pressure conditions in the WGS reactor may be selected in order to substantially optimize the operating conditions of the membrane separator (e.g. to maximize the separation of hydrogen in the membrane separator).

### **Embodiment example 2**

5 Figure 4 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 2. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may  
10 be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane and water condensation 7 may be as described with reference to Figure 3 with corresponding reference signs.

A difference between embodiment example 2 and embodiment example 1 is that the amine unit 8 of embodiment example 1 is replaced with cryogenic separation 13 of  
15 CO<sub>2</sub> 131 from the dried gas 73, giving the rest gas 132 for use in fired heater(s).

### **Embodiment example 3**

Figure 5 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 3. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming  
20 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. This embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such configuration allows the shifted  
25 gas 61 to be heated to the ideal temperature before entering the membrane unit as stream 71. In addition, reducing the water concentration before the membrane unit may advantageously increase the hydrogen concentration and may protect materials in the membrane unit.

The use of water condenser 7 on the gas output from the retentate side of the  
30 membrane separator 12 is optional.

CO<sub>2</sub> 81 is removed in an amine unit 8 leaving an energy rich rest gas 84.

#### Embodiment example 4

Figure 6 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 4. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

The present embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such a configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as stream 71.

CO<sub>2</sub> 131 is removed in the cryogenic unit 13 leaving an energy rich rest gas 132.

A comparison of the comparative example and embodiment examples 1-4 is provided below.

A comparison of performance of the comparative example and embodiment examples 1, 2, 3 and 4 is listed in Table 2 in Figure 11. There are, in addition, differences in investment and operating costs (i.e. CAPEX and OPEX). As to the investment costs, prices from vendors show that for hydrogen separation, PSA is considerably more costly than using a Pd-membrane, and that for CO<sub>2</sub> separation, using amine is significantly more costly than cryogenic separation. In addition, the footprints of PSA and amine are much larger than for Pd-membrane and cryogenic CO<sub>2</sub> separation.

Using a Pd-membrane, as in embodiment examples 1-4, is advantageous due to lower cost, smaller footprint and a higher hydrogen recovery factor than the comparative example. Note from the H<sub>2</sub> recovery factor that only 7% of the hydrogen in the shifted gas is lost in embodiment examples 1-4, compared to 14% in the comparative example. The percentage of carbon captured is above the 95% mark for embodiment examples 1 and 3, which is fully acceptable for most projects, although

these still use amine separation of CO<sub>2</sub>. The amine separation in these two embodiments is, however, significantly simpler than in the comparative example, due to the more than 3-fold higher concentration of CO<sub>2</sub> in the inlet gas. Other factors to be considered are the conversion in the WGS (see Table 2 in Figure 11), and differences in how water is condensed (see Table 1 in Figure 10 as well as the figures).

Known techniques are based on the assumption that a high conversion of CO in the WGS reactor results in better system performance with regard to hydrogen and CO<sub>2</sub> recovery. However, test of embodiments show that the performance of the separation technologies is more dominant on the overall system performance. Accordingly, operating the WGS at 300 °C is advantageous.

There is no condensation of water and heat exchange after WGS and before the Pd-membrane in Embodiment Examples 1 and 2, in contrast to Embodiment Examples 3 and 4. The discussed advantages are summarized in Table 3 in Figure 12. It follows that using a Pd-membrane is preferable compared the comparative example, and that there is no need to adjust temperature and knock out water directly after WGS.

### **Embodiment examples 5-7**

Figure 7 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment Examples 5-7.

The processes in embodiment Examples 5-7 may be substantially the same, or identical, to Embodiment Example 2 except that the rest gas 132 is recycled to the ATR 2.

The oxygen feed 51 may be adjusted to secure a constant exit temperature from ATR of about 1020 °C. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. The separation of hydrogen by a Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation 13 may be as described in Figure 4 with corresponding reference signs.

The only difference is that the rest gas 132 is used as recycle-gas to the ATR 2. The processes in the ATR 2 are therefore adapted so that the rest gas can additionally be received by the ATR 2.

5 The difference between Embodiment Examples 5-7 is in the amount of rest gas that is recycled, which is detailed in Table 4 in Figure 13.

### **Comparison of Embodiment Examples 2 and 5-7**

In Table 4 in Figure 13, Embodiment Examples 5-7, with recycle of rest gas, are compared to Embodiment Example 2. Although Embodiment Example 2 shows good performance, as seen in Table 3 in Figure 12, it is desirable to improve the efficiency of CO<sub>2</sub> capture and the carbon capture fraction. Embodiments achieve this by recycling at least part of the rest gas to the reformer section. The results outlined in Table 4, in Figure 13, show a surprising effect in that much better performances are reached. Hydrogen production increases, with a recovery of 99% for Embodiment Example 7 (90% recycle), compared to 93% H<sub>2</sub> recovery for Embodiment Example 2 as defined in Table 2 in Figure 11; a hydrogen loss is reduced from 7% to 1%. Simultaneously, the carbon capture increases from 90% in Embodiment Example 2 to 99% in Embodiment Example 7, the best performance of all examples.

When the production and separation efficiencies increase, more oxygen is needed in the ATR and less fuel gas is available for heat generation. The advantages summarized in Table 5, in Figure 14, indicates that a high degree of recycle is preferable. Probably more important is that a superior carbon capture fraction, as in Embodiment Example 7, is considered a decisive advantage in many hydrogen projects.

### **Embodiment Example 8**

25 Figure 8 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 8 which may be identical to Embodiment Example 2 except that the rest gas 133 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the WGS 6. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding

30

reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest gas 133 is used as recycle-gas to the WGS 6. Process simulations have been made for recycle of 50%, 80% and 90% of rest gas to WGS. However, embodiments include using any feasible recycle ratio of the rest gas.

### **Embodiment Example 9**

Figure 9 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 9 which may be identical to Embodiment Example 2 except that the rest gas 134 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the membrane unit 12. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by the Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest gas 134 is used as recycle-gas to the membrane unit 12. Process simulations have been made for recycle of 50%, 80% and 90% of rest gas to the Pd-membrane. However, embodiments include using any feasible recycle ratio of the rest gas.

### **Embodiment Example 10**

Embodiment Example 10 is identical to Embodiment Examples 5-7 except that the oxygen feed 51 is kept constant compared to Embodiment Example 2. This reduces the exit temperature from the ATR 2 from 1020 °C to, respectively, 1008 °C, 999 °C, 989 °C and 974 °C for 30%, 50%, 80% and 90% recycle.

### **Comparison of Embodiment Examples 2, 6, 8, 9 and 10**

Table 6, in Figure 15, summarizes 80% recycle of rest gas from CO<sub>2</sub> separation compared to no recycle. The recycle is to the ATR, WGS and Pd-membrane



respectively. For recycle to ATR, the oxygen feed has been increased in Embodiment Example 6 to keep the exit temperature constant. The following surprising advantageous effects are found:

- Hydrogen production increases significantly for all recycle cases.
- 5 • Carbon capture rate increases significantly for all recycle cases.
- Very high capture rates are obtained when recycle is to ATR or WGS.
- Recycle to ATR without increasing oxygen flow is beneficial.
- More energy for fired heater is available when recycle is to Pd-membrane.

### **Embodiment Example 11**

10 Figure 16 shows a system according to Embodiment Example 11.

Embodiment Example 11 is directed towards producing ammonia 141 and is similar to all previous Embodiment Examples in that a Pd-membrane 12 is used to separate hydrogen, the syngas is produced by a combination of GHR 1 and ATR 2, and there is a WGS reactor(s) 6.

15 In the present embodiment, nitrogen 52, from the ASU 5, is combined with hydrogen, from the membrane separator 12, in an ammonia synthesis unit 14. The hydrogen supplied to the ammonia synthesis unit 14 may be either hydrogen stream 121 or the compressed hydrogen stream 111.

A preferred implementation of the present embodiment is shown in Figure 16. This is  
20 similar to Embodiment Example 8 and has corresponding reference signs. However, embodiments also include alternatively generating the hydrogen supply using any of the other Embodiment Examples described herein, and using any recycle ratios of rest gas.

Advantages of using systems according to the present embodiment for the  
25 production of ammonia include, but are not limited to, efficient natural gas reforming by using GHR/ASU, one-step WGS reaction, hydrogen separation at the same temperature as WGS, ease of separating CO<sub>2</sub> by cryogenic cooling, high hydrogen productivity and low CO<sub>2</sub> emission by recycle of rest gas, and low content of inerts in the ammonia synthesis loop.

## Embodiment Example 12

The present embodiment is directed towards providing performance gains by recycling the rest gas that remains after the hydrogen and CO<sub>2</sub> separation processes.

In the present embodiment, the hydrogen separation process may be performed  
 5 before the CO<sub>2</sub> separation process, and the rest gas is therefore the gas remaining after the CO<sub>2</sub> separation process. The present embodiment also includes an alternative implementation in which the CO<sub>2</sub> separation process is performed before the hydrogen separation process, and the rest gas is therefore the gas remaining after the hydrogen separation process.

10 The rest gas may be fed back into one or more of any of the processes performed in the hydrogen production process. For example, the rest gas may be fed back into one or more reforming process, water-gas-shift process, hydrogen separation process and CO<sub>2</sub> separation process.

All of the rest gas may be recycled by feeding it back into one or more of the  
 15 processes performed in the hydrogen production process. Alternatively, only a portion of the rest gas may be recycled. The portion of the rest gas that is recycled may be at least 50%, preferably at least 80%, and more preferably at least 90%.

In the present embodiment, any reforming process may be used. In particular, the reforming process may only comprise an autothermal reforming process.

20 In the present embodiment, any hydrogen separation process and CO<sub>2</sub> separation process may be used. In particular, the hydrogen separation process may be a PSA process. The CO<sub>2</sub> separation process may be a cryogenic process.

In the present embodiment, the hydrogen separation process is not restricted to being performed before the CO<sub>2</sub> separation process. Embodiments include the CO<sub>2</sub>  
 25 separation process alternatively being performed before the hydrogen separation process and the rest gas being the remaining gas following the hydrogen separation process. Some, or all, of the rest gas may be recycled as described above.

The embodiments presented throughout the present document provide advantageous methods and systems for the production of hydrogen and/or ammonia.

30 In particular, the use of a Pd-membrane to separate hydrogen immediately

downstream of a WGS reactor has a surprising synergistic effect. Contrary to known techniques, the WGS reactor may be operated at substantially the same temperature as the Pd-membrane. The WGS reactor may be operated under conditions that are more preferable for the effective operation of the Pd-membrane and this can substantially improve the overall efficiencies and effectiveness of the system.

In a particularly preferred implementation according to an embodiment, the hydrogen separation process uses a hydrogen separation device as disclosed in the published patent application WO2020/012018A1, the entire contents of which are incorporated herein by reference. The hydrogen separation device disclosed in WO2020/012018A1 uses Pd-membranes to separate hydrogen from a gas mixture. The operational capabilities of the hydrogen separation device disclosed in WO2020/012018A1 result in it being particularly suitable for use in the hydrogen and/or ammonia production processes according to embodiments.

Other particularly advantageous techniques that may be used in methods and systems according to embodiments are the recycling of the rest gas directly to the Pd-membrane separator and/or water gas shift (WGS) reactor.

Embodiments include a number of modifications and variations to the above described techniques.

Embodiments may use a Pd-membrane separator 12 to separate hydrogen from shifted gas. Optionally, a sweep gas may be used on the permeate side of the membrane. The sweep gas may be steam. The steam may be at an elevated total pressure above 5 bar, preferably above 10 bar.

Embodiments include the use of a water separator, such as a condenser, in between the Pd-membrane separator 12 and the hydrogen compressor 11 to separate hydrogen from the used sweep gas.

Embodiments also include optionally using a sweep gas on the retentate side of the membrane.

In embodiments, a) sulfur may be removed from the feed gas, b) the feed gas may be saturated with water, c) hydrogen may optionally be added to the gas stream before pre-reforming the gas that has been subject to treatments a and b, d) the gas from c may be reformed by a combination of gas-heated reforming and autothermal

- reforming, e) the reformed gas may be subjected to water-gas-shift to give a shifted gas, f) hydrogen may be separated from the shifted gas using a Pd-membrane, g) carbon dioxide may be separated from the shifted gas that has been subject to treatment f, h) the separated hydrogen is optionally compressed and liquefied, i) the
- 5 separated carbon dioxide is optionally compressed and liquefied.

In embodiments, at least part of the rest gas from separating hydrogen and carbon dioxide may be recycled.

- In embodiments, the portion of the rest gas that is recycled may be more than 50%, preferably around 80%, more preferably at least 90%. Embodiments include all of the
- 10 rest being recycled.

In embodiments, the rest gas that is recycled may be fed back into the gas-heated reforming process.

In embodiments, the rest gas that is recycled may be fed back into the autothermal reformer, the water-gas-shift reactor(s) and/or the Pd-membrane.

- 15 In embodiments, the feed gas may be natural gas.

In embodiments, the feed gas may be a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.

In embodiments, the gas-heated reformer may be heated by the exit gas from an autothermal reformer.

- 20 In embodiments, the exit temperature of the reformed gas from the gas-heated reformer may be in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

In embodiments, the autothermal reformer may be supplied with oxygen from an air separation unit.

- 25 In embodiments, the autothermal reformer may be supplied with oxygen or oxygen enriched air from a membrane air separation unit.

In embodiments, the water-gas-shift reaction may be conducted in a high-temperature-shift and a low-temperature shift reactor.

In embodiments, the water-gas-shift reaction may be conducted in one reactor.

In embodiments, the water-gas shift reactor may be operated at a temperature between 200 and 300 °C, preferably between 240 and 270 °C.

In embodiments, the water-gas shift reactor may be operated at a temperature between 270 and 330 °C, preferably between 290 and 310 °C, most preferably at about 300 °C.

In embodiments, no additional steam may be added between the reformer and the WGS-reactor.

In embodiments, the water-gas shift reactor may utilize a Cu-based catalyst.

In embodiments, the CO conversion in the WGS reactor may be at least 90%, but below 98%, more preferably below 96%.

In embodiments, hydrogen may be separated before CO<sub>2</sub> is separated from the shifted gas.

In embodiments, the WGS and the Pd-membrane may be operated at about the same temperature.

In embodiments, water may be separated after the Pd-membrane and not before the membrane.

In embodiments, the Pd-membrane may be operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

In embodiments, carbon dioxide may be separated cryogenically. The carbon dioxide may be deposited in a geological reservoir.

In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by a nearby processing plant.

In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by electricity from the grid and/or electricity from renewable energy source(s).

In embodiments, nitrogen may be produced by the air separation unit.

In embodiments, nitrogen and hydrogen may be used to produce ammonia. In embodiments, methanisation may be substantially avoided in the ammonia synthesis.

Embodiments include the following numbered clauses:

1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

5

performing reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide, wherein

10

the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process, and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

15

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process to thereby generate hydrogen and a hydrogen-depleted shifted gas; and

20

performing a carbon dioxide separation process on the hydrogen-depleted shifted gas to thereby generate carbon dioxide;

wherein the hydrogen separation process comprises:

25

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

30

outputting hydrogen from the permeate side of the Palladium membrane; and

outputting hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

- 5        2. The method according to clause 1, further comprising performing a sulfur removal process on the feed gas before performing the reforming processes on the feed gas.
- 10       3. The method according to clause 1 or 2, further comprising performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; and  
  
the method further comprising:  
  
15       optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and  
  
optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.  
  
20       4. The method according to any of the preceding clauses, wherein the carbon dioxide separation process generates carbon dioxide and a rest gas, and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one of said performed processes in the  
25       method of producing hydrogen.
- 30       5. The method according to clause 4, wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.
- 35       6. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the autothermal reforming process.
7. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the water-gas-shift process.

8. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
- 5 9. The method according to any of the preceding clauses, wherein the feed gas is natural gas.
10. The method according to any of the preceding clauses, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
- 10 11. The method according to any of the preceding clauses, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.
- 15 12. The method according to any of the preceding clauses, wherein the autothermal reforming process is supplied with oxygen from an air separation unit.
- 20 13. The method according to any preceding clause, wherein the water-gas-shift process is conducted in one water-gas-shift reactor.
14. The method according to clause 13, wherein the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C.
- 25 15. The method according to any of the preceding clauses, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.
- 30 16. The method according to any of the preceding clauses, wherein no additional steam is added between the reforming processes and the water-gas-shift process.
- 35



17. The method according to any of the preceding clauses, wherein the water-gas-shift process comprises using a Cu-based catalyst.

18. The method according to any of the preceding clauses, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

19. The method according to any of the preceding clauses, wherein water is separated from the hydrogen-depleted shifted gas output from the hydrogen separation process.

20. The method according to any of the preceding clauses, wherein water is not separated from the shifted gas before the hydrogen separation process.

21. The method according to any of the preceding clauses, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

22. The method according to any of the preceding clauses, wherein the carbon dioxide separation process is conducted cryogenically.

23. The method according to clause 12, or any clause dependent thereon, wherein the air separation unit is also arranged to generate nitrogen, and the method comprises generating ammonia in dependence on nitrogen output from the air separation unit and hydrogen output from the hydrogen separation process.

24. A hydrogen production plant arranged to perform the method of any of clauses 1 to 22.

25. An ammonia production plant arranged to perform the method of clause 23.

The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather, the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary

embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without departing from the spirit and scope of the invention as set forth in the appended claims.

**Claims:**

1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

- 5 performing a reforming process on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

10

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and

- 15 the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the reforming process, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

- 20 wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.

2. The method according to claim 1, wherein the reforming process comprises an autothermal reforming process.

25

3. The method according to claim 1 or 2, wherein the reforming process comprises a gas heated reforming process.

4. The method according to any preceding claim, wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and

5 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

5. The method according to any preceding claim, further comprising:

10 optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and

optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;

15 wherein the pre-reforming process comprises:

optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and

20 optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

6. The method according to any preceding claim, wherein the hydrogen separation process comprises:

25 inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

30 outputting hydrogen from the permeate side of the Palladium membrane; and

outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

7. The method according to any preceding claim, wherein the hydrogen separation process comprises a PSA process.
8. The method according to claims 2 or 4, or any claim dependent thereon, wherein the rest gas that is recycled is fed back into the autothermal reforming process.
9. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the water-gas-shift process.
10. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
11. The method according to any of the preceding claims, wherein the feed gas is natural gas.
12. The method according to any of the preceding claims, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
13. The method according to claim 3, or any claim dependent thereon, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.
14. The method according to any of claims 2 or 4, or any claim dependent thereon, wherein the autothermal reforming process is supplied with oxygen from an air separation unit.
15. The method according to any preceding claim, wherein the water-gas-shift process is conducted in one water-gas-shift reactor;

wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C; and

5

wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

10

16. The method according to any preceding claim, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

15

17. The method according to any preceding claim, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

18. The method according to any preceding claim, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

20

19. The method according to any preceding claim, wherein water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

25

20. The method according to any preceding claim, wherein water is not separated from the shifted gas before the hydrogen separation process.

30

21. The method according to claim 6, or any claim dependent thereon, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

22. The method according to any of the preceding claims, wherein the carbon dioxide separation process is conducted cryogenically.

23. The method according to any preceding claim, the method further comprising generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

5 24. A hydrogen production plant arranged to perform the method of any of claims 1 to 22.

25. An ammonia production plant arranged to perform the method of claim 23.

**Abstract**

Disclosed herein is a method of producing hydrogen, the method comprising:

5 receiving a feed gas comprising hydrocarbons; performing a reforming process on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process and a carbon dioxide separation process on the shifted

10 gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the reforming process, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process; wherein the portion of the rest gas that is recycled is at least

15 50%, preferably at least 80%, and more preferably at least 90%.

[Fig. 9]



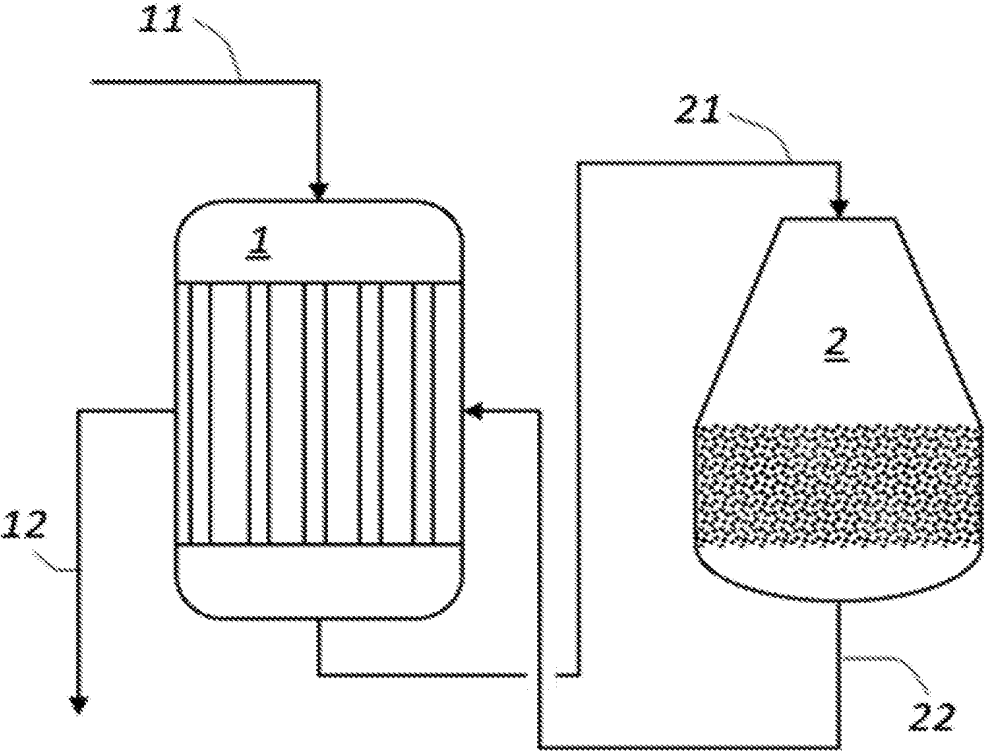


FIGURE 1

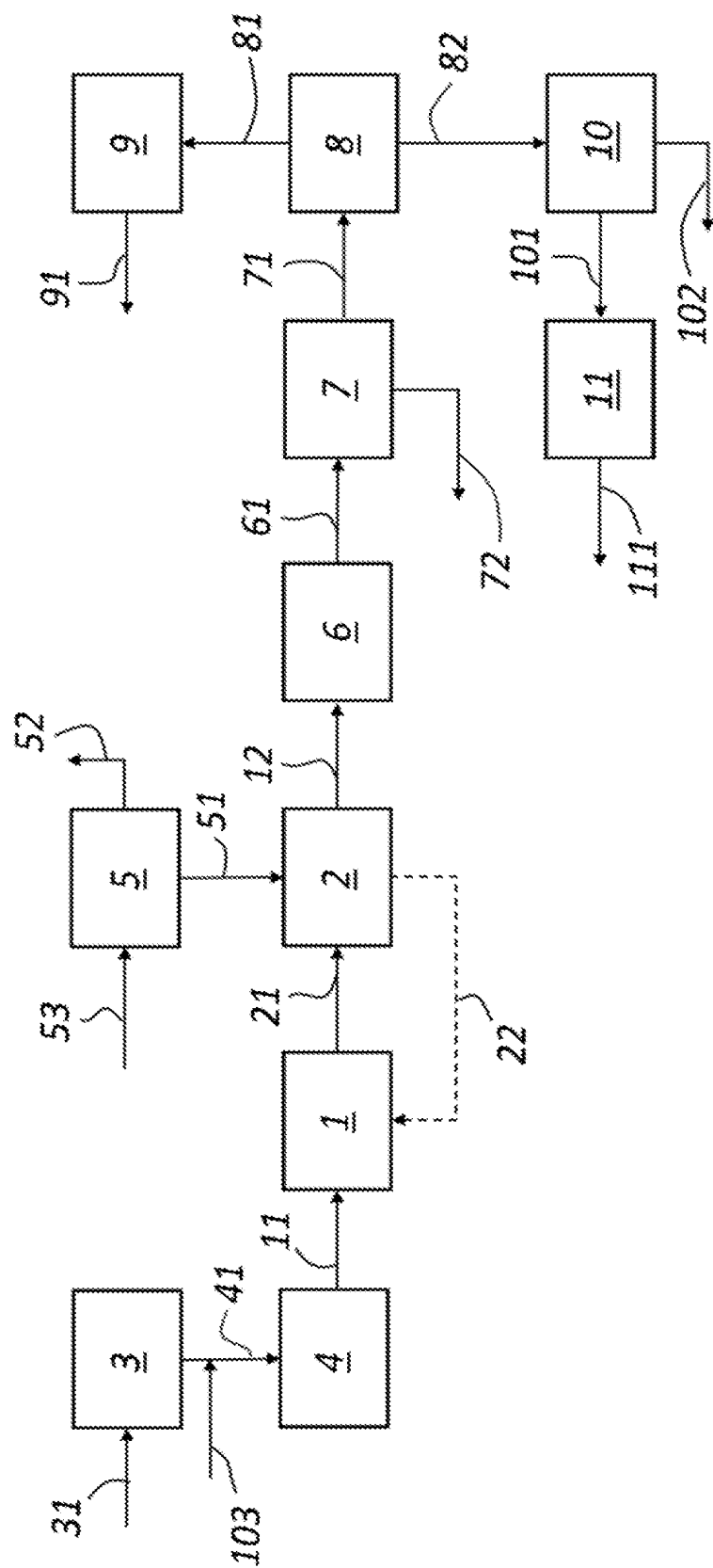
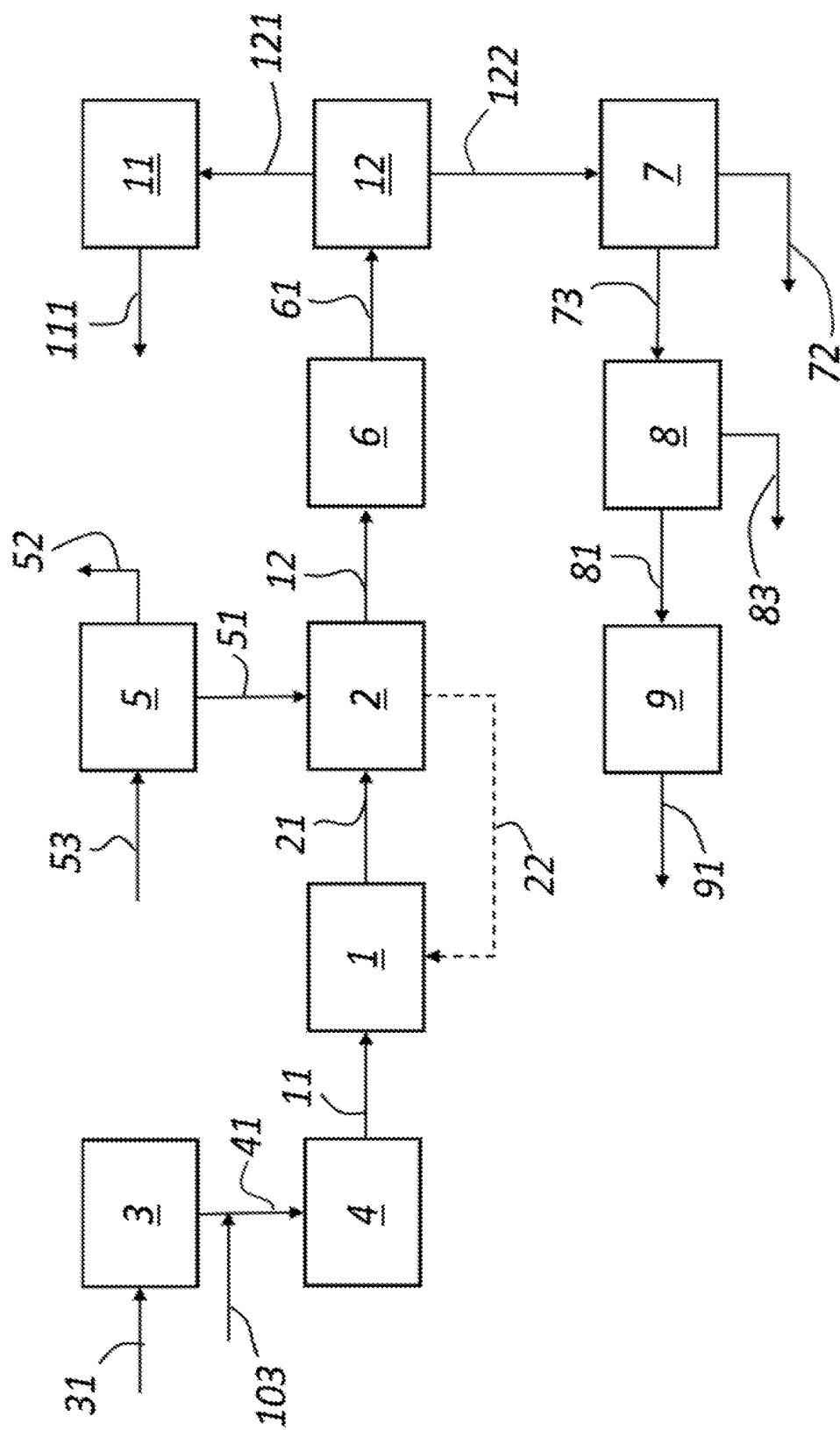


FIGURE 2



## FIGURE 3

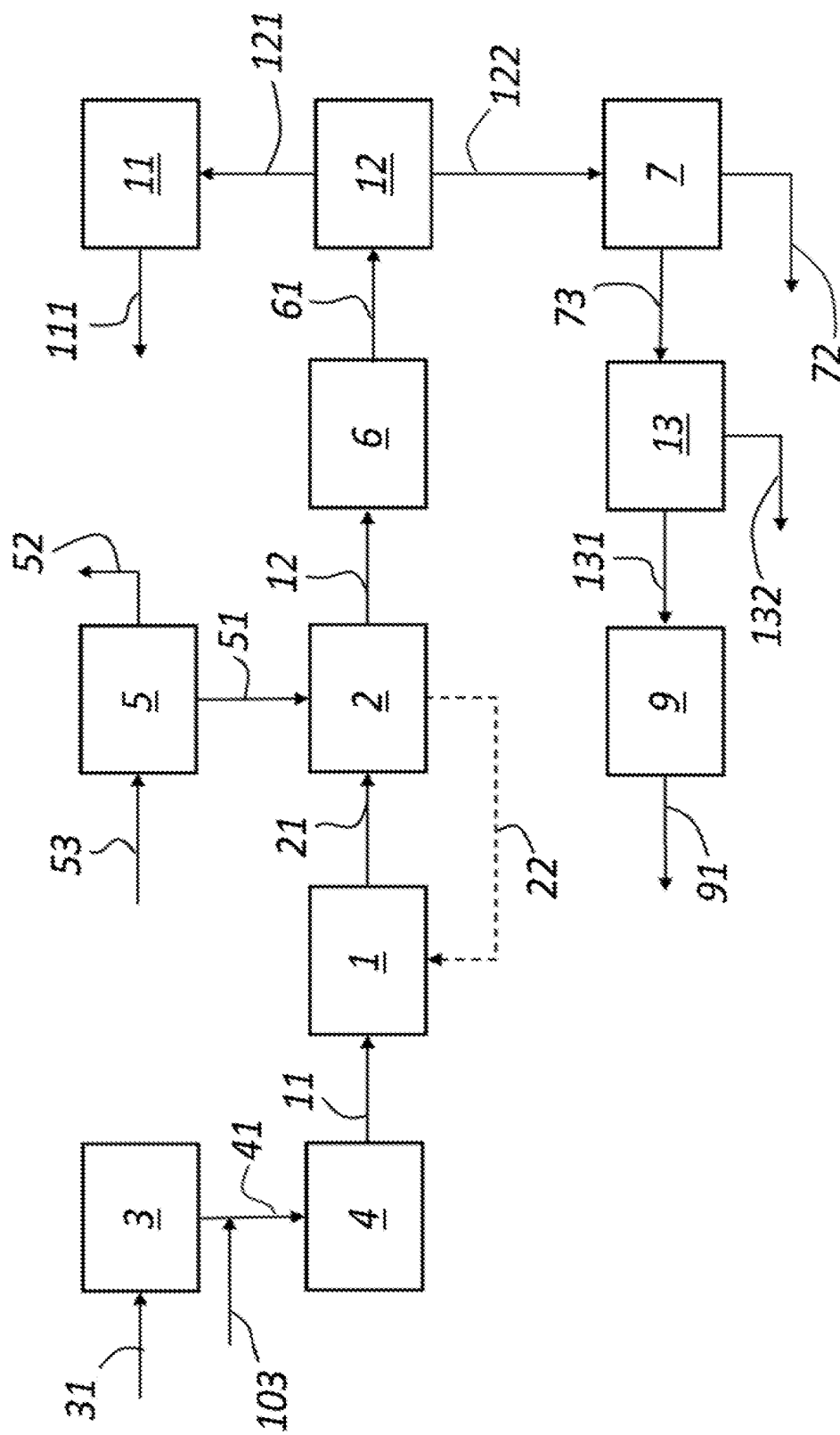


FIGURE 4

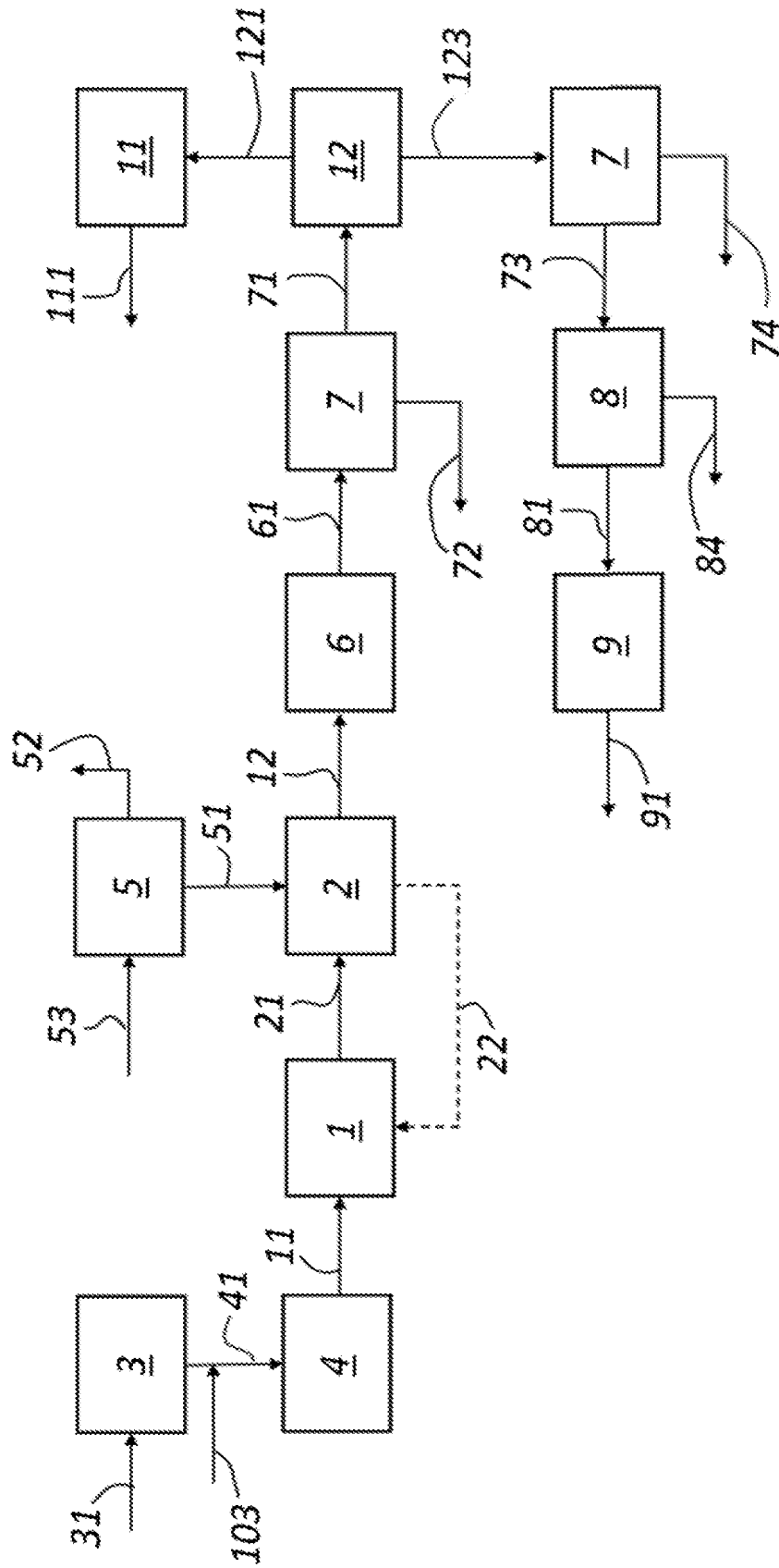


FIGURE 5

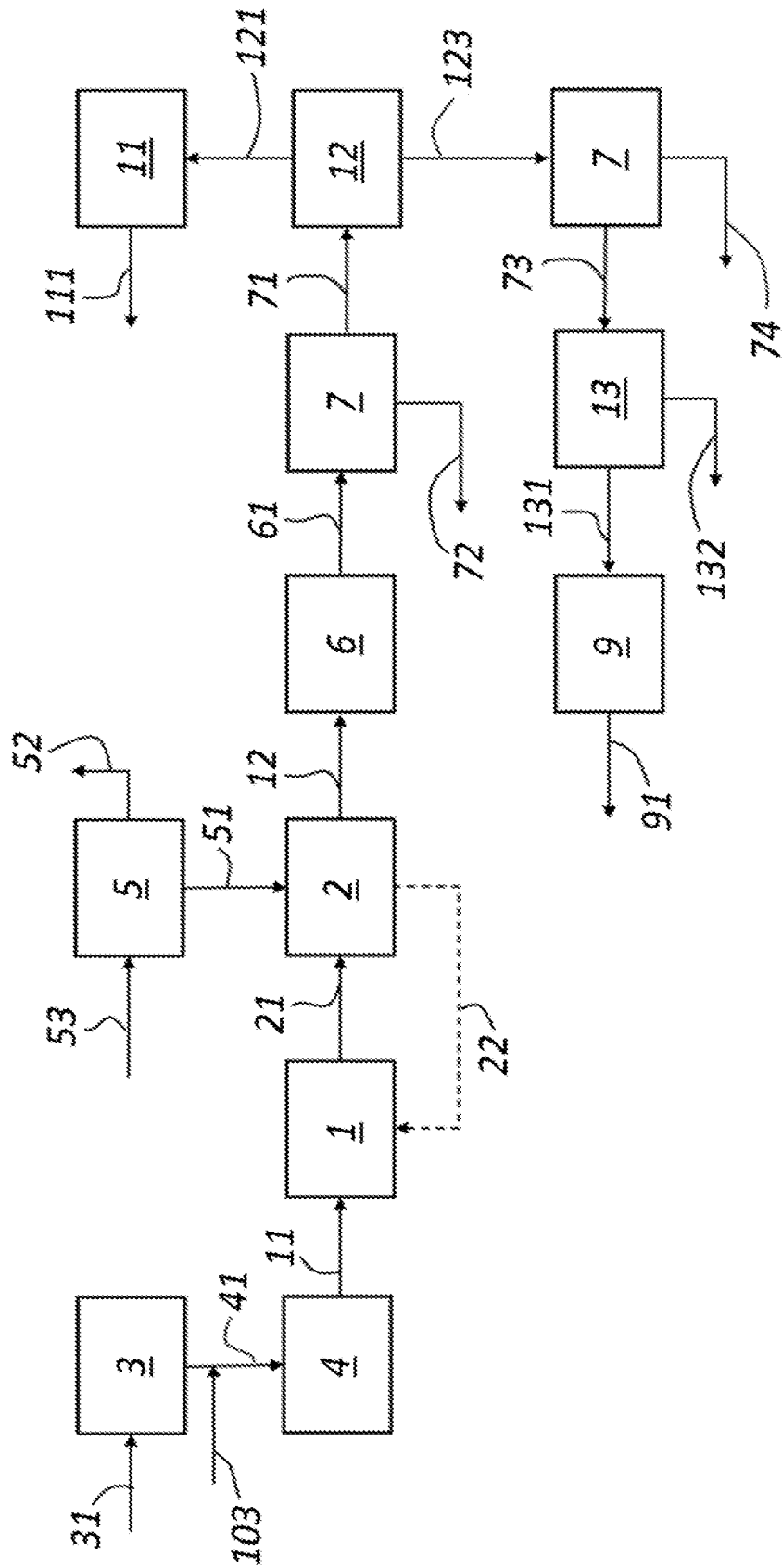
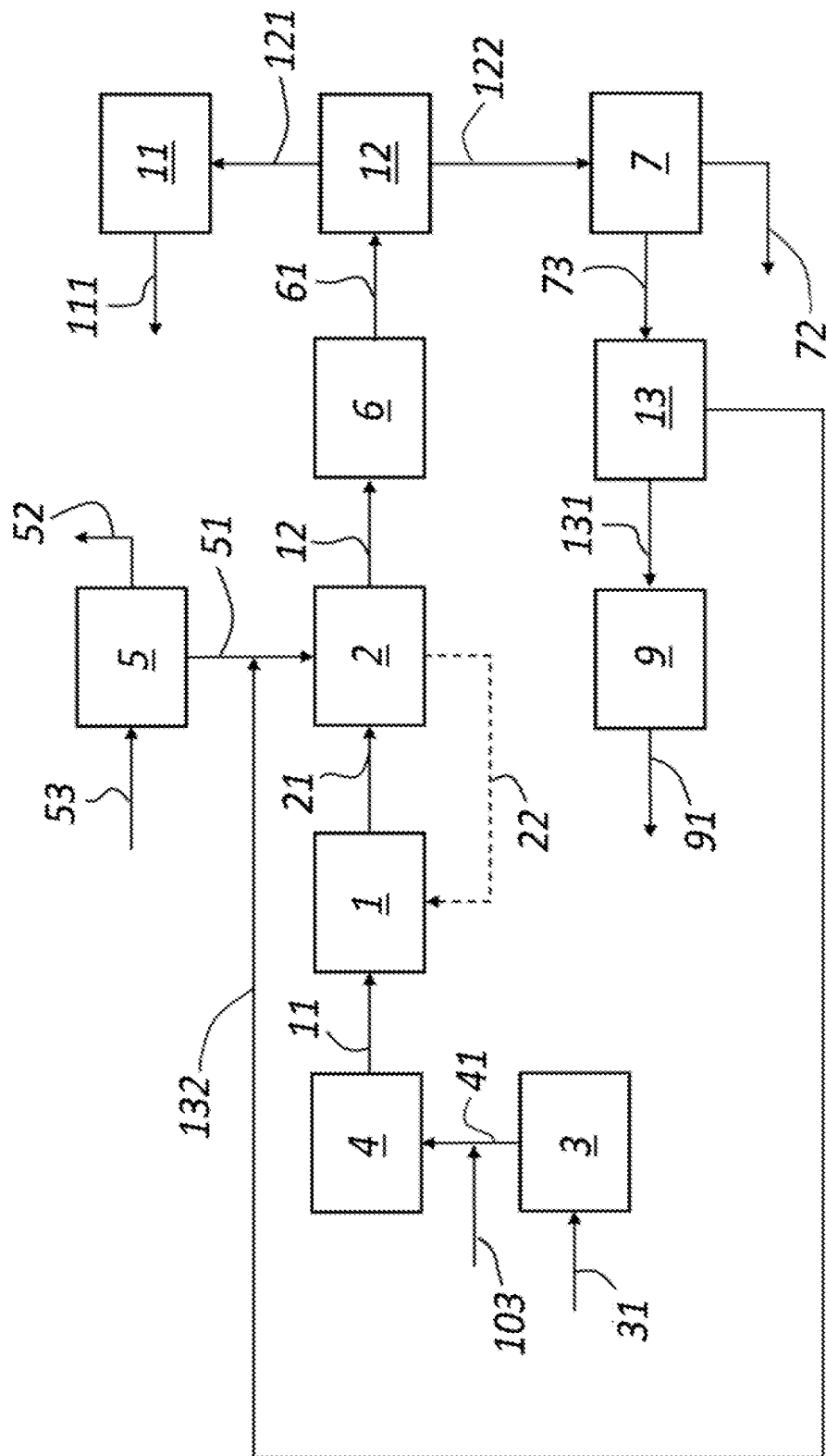


FIGURE 6



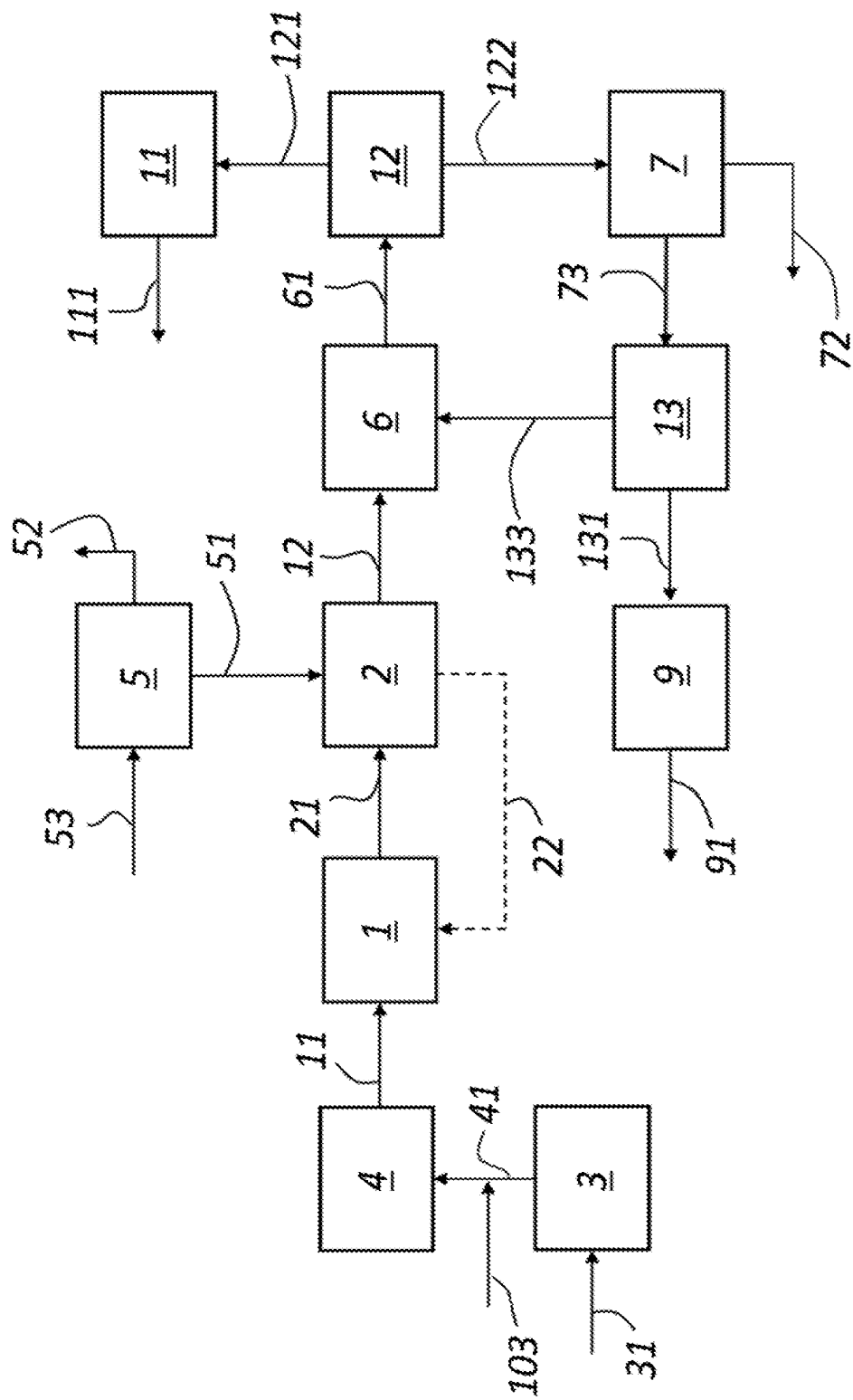


FIGURE 8



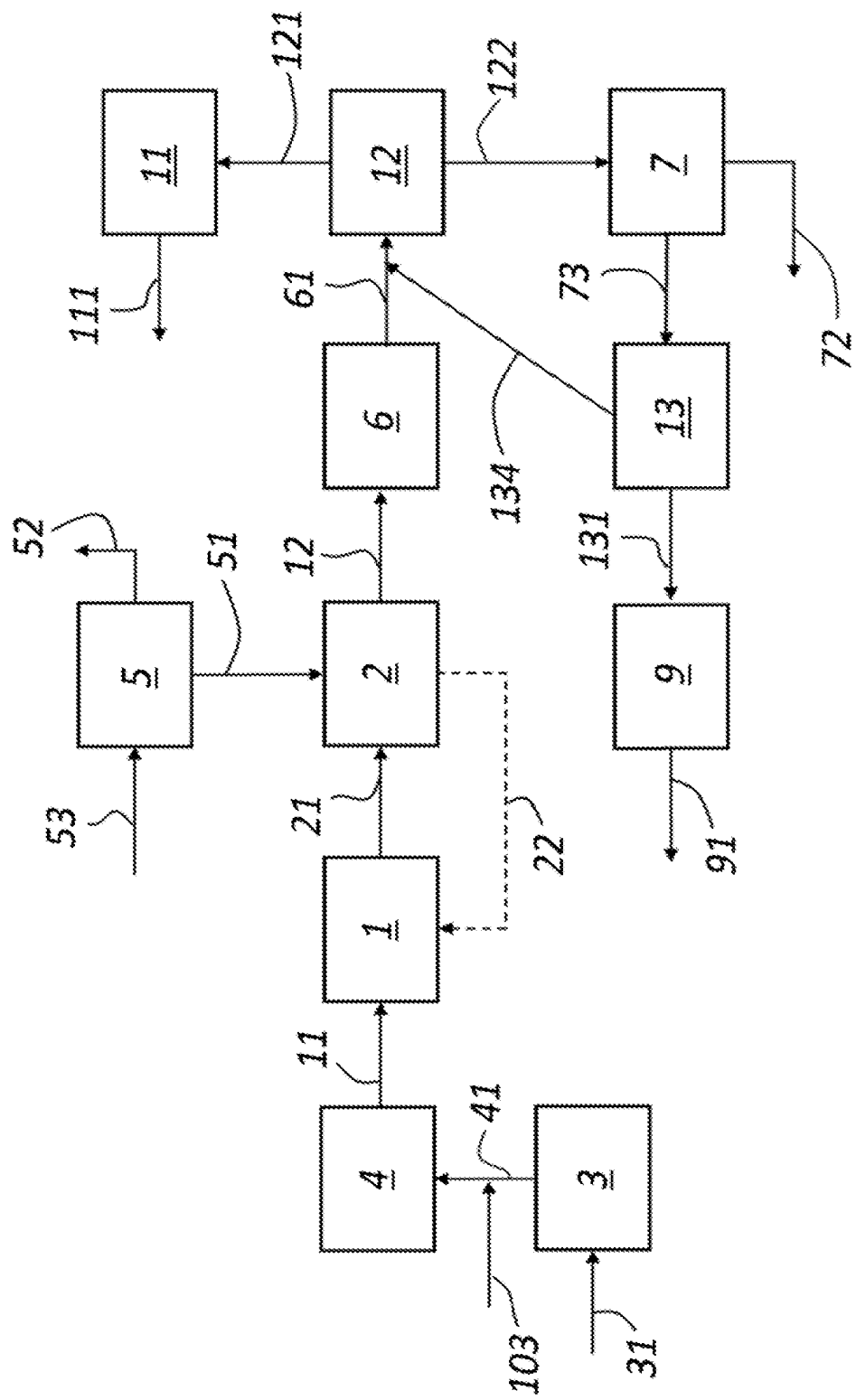


FIGURE 9

Table 1. Summary of process schemes.

|                                          | Comparative<br>Example | Embodiment<br>Example 1 | Embodiment<br>Example 2 | Embodiment<br>Example 3 | Embodiment<br>Example 4 | Embodiment<br>Examples 5-<br>7 |
|------------------------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------|
| WGS temperature<br>(°C)                  | 256                    | 300                     | 300                     | 256                     | 256                     | 300                            |
| Pd membrane                              |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Water condensation<br>directly after WGS | ✓                      |                         |                         | ✓                       | ✓                       |                                |
| Water condensation<br>after membrane     |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Amine separation                         | ✓                      | ✓                       |                         | ✓                       |                         |                                |
| Cryogenic<br>separation                  |                        |                         | ✓                       |                         | ✓                       | ✓                              |
| PSA                                      | ✓                      |                         |                         |                         |                         |                                |
| Recycle of rest-gas                      |                        |                         |                         |                         |                         | ✓                              |

FIGURE 10

Table 2.

| Type                                   | Comparative Example | Embodiment Example 1 | Embodiment Example 2  | Embodiment Example 3  | Embodiment Example 4  |
|----------------------------------------|---------------------|----------------------|-----------------------|-----------------------|-----------------------|
|                                        |                     | Membrane after WGS   | Membrane after heater | Membrane after heater | Membrane after heater |
|                                        | Base case           | Pd + Amine           | Pd + Cryo             | Pd + Amine            | Pd + Cryo             |
| H <sub>2</sub> production (kg/h)       | 1412                | 1516                 | 1516                  | 1524                  | 1524                  |
| H <sub>2</sub> production (kmol/h)     | 701                 | 752                  | 752                   | 756                   | 756                   |
| H <sub>2</sub> recovery factor (%)     | 86                  | 93                   | 93                    | 93                    | 93                    |
| Carbon capture (%) <sup>*</sup>        | 97.5                | 96                   | 90                    | 96                    | 90                    |
| CO <sub>2</sub> before capture (mol%)  | 25                  | 79                   | 79                    | 80                    | 80                    |
| Purity of CO <sub>2</sub> captured (%) | 100                 | 100                  | 99.9                  | 100                   | 99.9                  |
| CO conversion in WGS                   | 97.4                | 95.0                 | 95.0                  | 97.4                  | 97.4                  |

<sup>\*</sup> Defined as carbon captured relative to carbon in feed

FIGURE 11

Table 3. Advantages of the different examples.

| Type                                    | Comparative Example | Embodiment Example 1 | Embodiment Example 2 | Embodiment Example 3  | Embodiment Example 4 |
|-----------------------------------------|---------------------|----------------------|----------------------|-----------------------|----------------------|
|                                         |                     | Membrane after WGS   |                      | Membrane after heater |                      |
|                                         | Base case           | Pd + Amine           | Pd + Cryo            | Pd + Amine            | Pd + Cryo            |
| Cost of H <sub>2</sub> separation       |                     | +++                  | +++                  | +++                   | +++                  |
| Footprint of H <sub>2</sub> separation  |                     | ++                   | ++                   | ++                    | ++                   |
| Efficiency of H <sub>2</sub> separation |                     | +++                  | +++                  | +++                   | +++                  |
| Cost of CO <sub>2</sub> separation      |                     | +                    | ++                   | +                     | ++                   |
| Footprint of CO <sub>2</sub> separation |                     | +                    | ++                   | +                     | ++                   |
| Efficiency of CO <sub>2</sub> capture   | ++                  | +                    |                      | +                     |                      |
| Water condensation                      | ++                  | ++                   | ++                   |                       |                      |
| Heat exchange                           | ++                  | +                    | +                    |                       |                      |
| Total                                   | 6+                  | 14+                  | 15+                  | 11+                   | 12+                  |

FIGURE 12

Table 4. Effect of recycling rest-gas to ATR.

|                                     | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Recycle option                      | No recycle              | 50%                     | 80%                     | 90%                     |
| O <sub>2</sub> to ATR (kg/h)        | 4179                    | 4316                    | 4426                    | 4482                    |
| H <sub>2</sub> production (kmol/h)  | 752                     | 777                     | 794                     | 799*                    |
| Carbon capture (%)                  | 89.7                    | 94.4                    | 97.7                    | 98.8                    |
| Heat available in Fired heater (MW) | 4.6                     | 2.5                     | 1.0                     | 0.5                     |

\* Represents 99% hydrogen recovery compared to Table 2.

FIGURE 13

Table 5. Advantages of Embodiment Examples 5-7.

|                                         | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|                                         | No recycle              | 50 %                    | 80 %                    | 90 %                    |
| Cost of H <sub>2</sub> separation       | +++                     | +++                     | +++                     | +++                     |
| Footprint of H <sub>2</sub> separation  | ++                      | ++                      | ++                      | ++                      |
| Efficiency of H <sub>2</sub> separation | +++                     | +++                     | ++++                    | ++++                    |
| Cost of CO <sub>2</sub> separation      | ++                      | ++                      | ++                      | ++                      |
| Footprint of CO <sub>2</sub> separation | ++                      | ++                      | ++                      | ++                      |
| Efficiency of CO <sub>2</sub> capture   |                         | +                       | ++                      | +++                     |
| Water condensation                      | ++                      | ++                      | ++                      | ++                      |
| Heat exchange                           | +                       | +                       | +                       | +                       |
| Energy efficiency                       | ++                      | +                       |                         |                         |
| Total                                   | 17+                     | 17+                     | 18+                     | 19+                     |

FIGURE 14

Table 6. Effect of recycling 80% rest-gas compared to no recycle.

|                                        | Embodiment<br>Example 2 | Embodiment<br>Example 6 | Embodiment<br>Example 8 | Embodiment<br>Example 9 | Embodiment<br>Example 10 |
|----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| Recycle option                         | No recycle              | To ATR                  | To WGS                  | To<br>membrane          | To ATR                   |
| Recycle ratio                          | 0%                      | 80%                     | 80%                     | 80%                     | 80%                      |
| O <sub>2</sub> to ATR (kg/h)           | 4179                    | 4426                    | 4179                    | 4179                    | 4179                     |
| ATR exit (°C)                          | 1020                    | 1020                    | 1020                    | 1020                    | 989                      |
| H <sub>2</sub> production (kmol/h)     | 752                     | 798                     | 803                     | 797                     | 807                      |
| Carbon capture (%)                     | 89.7                    | 97.7                    | 97,3                    | 95,1                    | 97,5                     |
| Heat available in Fired<br>heater (MW) | 4.6                     | 1.0                     | 1,5                     | 1,9                     | 1.2                      |

FIGURE 15

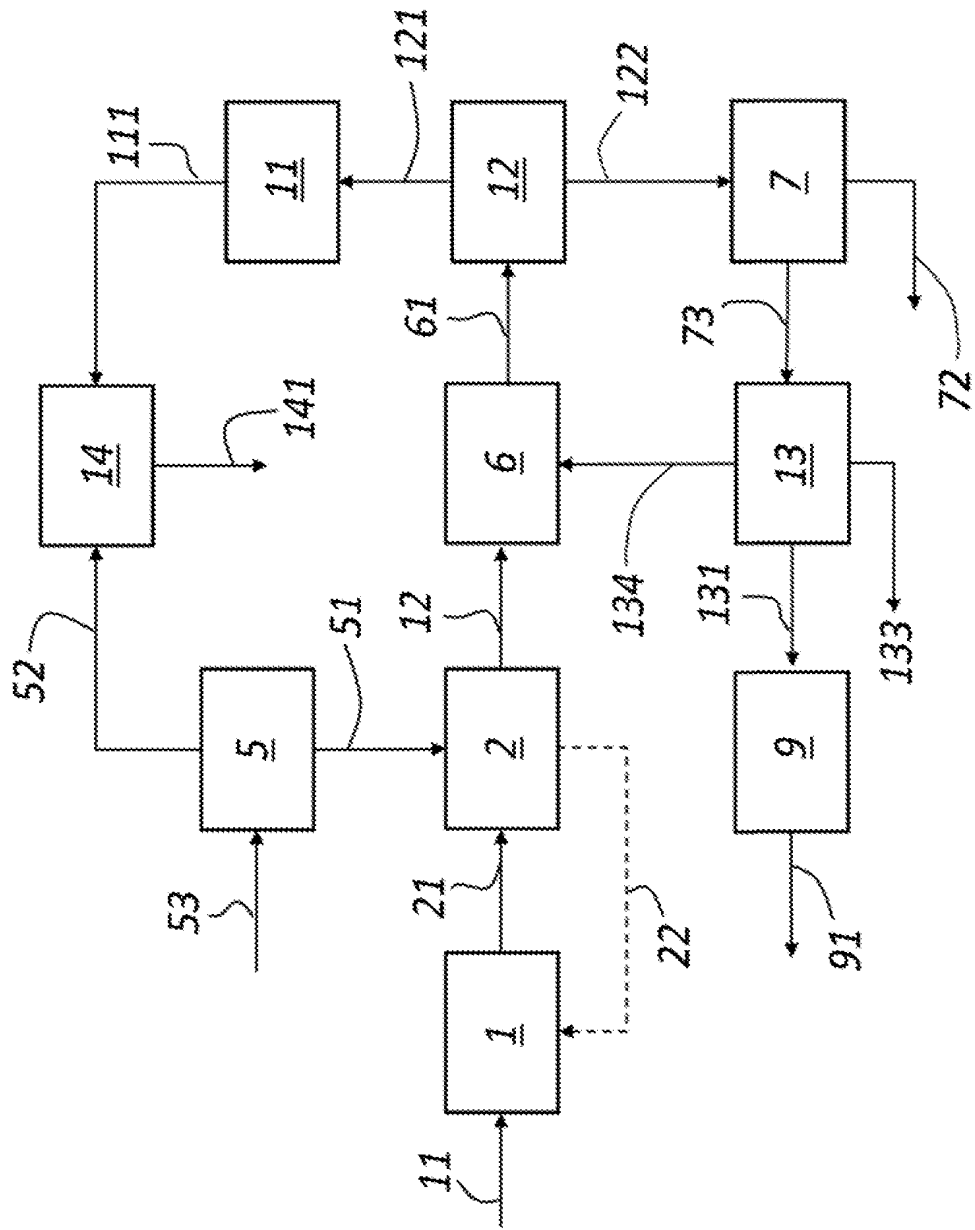


FIGURE 16



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|                                              |                                               |
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| International application number:            | <b>PCT/EP2021/054441</b>                      |
| International filing date:                   | <b>23 February 2021 (23.02.2021)</b>          |
| Document type:                               | <b>Certified copy of priority document</b>    |
| Document details:                            | Country/Office: <b>GB</b>                     |
|                                              | Number: <b>2010174.7</b>                      |
|                                              | Filing date: <b>02 July 2020 (02.07.2020)</b> |
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Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

*Application number* GB 2003317.1

|                                                                                                                                                                                                                                                   |                                                                                                                                   |                                  |                                               |
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| 2. Full name, address and postcode of the applicant or of each applicant                                                                                                                                                                          | <b>Reinertsen New Energy AS<br/>Leiv Eiriksson Senter<br/>Trondheim 7010<br/>Norway</b>                                           |                                  |                                               |
| Patents ADP number <i>(if you know it)</i>                                                                                                                                                                                                        |                                                                                                                                   |                                  |                                               |
| 3. Title of the invention                                                                                                                                                                                                                         | <b>HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS</b>                                                                                 |                                  |                                               |
| 4. Name of your agent <i>(if you have one)</i><br>"Address for service" to which all correspondence should be sent. This may be in the European Economic area or Channel Islands (see warning note below)<br><i>(including the postcode)</i>      | <b>J A Kemp LLP<br/>J A Kemp LLP<br/>14 South Square<br/>Gray's Inn<br/>London WC1R 5JJ<br/>Greater London<br/>United Kingdom</b> |                                  |                                               |
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Description: **28**

Claim(s): **4**

Abstract: **1**

Drawing(s): **16**

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| 12. Name, e-mail address, telephone, fax and/or mobile number, if any, of a contact point for the applicant | <b>HUNT-GRUBBE, Henry<br/>Email: hhunt-grubbe@jakemp.com<br/>Telephone: +44 20 3077 8600<br/>Fax: +44 20 7430 1000</b> |
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## HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### FIELD

The present disclosure relates to hydrogen and ammonia production processes. Embodiments provide a particularly efficient system for generating syngas and then  
5 separating hydrogen from the syngas using a membrane separator. The system according to embodiments may also use the separated hydrogen to generate ammonia.

### BACKGROUND

- 10 It is generally believed that the greenhouse effect and the climate on Earth are closely linked to human-made emissions of carbon dioxide (CO<sub>2</sub>). These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines. A desirable goal is to reduce the emission of CO<sub>2</sub> to the atmosphere. It is known art to reduce the  
15 emission of CO<sub>2</sub> from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen and carbon dioxide. These components are then separated, after which hydrogen may be used in a number of applications, such as electricity generation, heat generation and in different types of transportation. Hydrogen may also be mixed with natural gas to  
20 produce methane, a fuel for domestic and industrial energy users. Carbon dioxide has industrial applications but may also be deposited after compression to a desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.
- 25 Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen that is made by splitting water through electrolysis and compressed to typically 700 bar. Liquid hydrogen is being considered for heavier  
30 transport like ships and trains. Unfortunately, electrolysis has been calculated to be at least twice as costly as producing hydrogen by reforming natural gas. These

calculations include costs of separation and liquefaction of coproduced CO<sub>2</sub> and payment of tariffs for deposition of CO<sub>2</sub> in underground reservoirs. Another complicated issue with water electrolysis is calculation of the greenhouse effect, as most electricity is still produced from hydrocarbons with significant emission of CO<sub>2</sub> to the atmosphere. Therefore, producing hydrogen from natural gas with CO<sub>2</sub> storage is a significantly better option.

There is a general need to improve hydrogen production processes.

## SUMMARY OF INVENTION

According to first aspect of the present invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; performing reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide, wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process, and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process to thereby generate hydrogen and a hydrogen-depleted shifted gas; and performing a carbon dioxide separation process on the hydrogen-depleted shifted gas to thereby generate carbon dioxide; wherein the hydrogen separation process comprises: inputting the shifted gas to a hydrogen separator that comprises a palladium membrane, wherein the hydrogen separator comprises a permeate side of the palladium membrane and a retentate side of the palladium membrane, and the shifted gas is input to the retentate side of the palladium membrane; outputting hydrogen from the permeate side of the palladium membrane; and outputting hydrogen-depleted shifted gas from the retentate side of the palladium membrane.

Preferably, the method further comprises performing a sulfur removal process on the feed gas before performing the reforming processes on the feed gas.

Preferably, the method further comprises performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; and the method

further comprises: optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

- 5 Preferably, the carbon dioxide separation process generates carbon dioxide and a rest gas, and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one of said performed processes in the method of producing hydrogen.

10 Preferably, the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.

Preferably, the rest gas that is recycled is fed back into the autothermal reforming process.

Preferably, the rest gas that is recycled is fed back into the water-gas-shift process.

15 Preferably, the rest gas that is recycled is fed back into the hydrogen separation process.

Preferably, the feed gas is natural gas.

Preferably, the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.

20 Preferably, the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

Preferably, the autothermal reforming process is supplied with oxygen from an air separation unit.

Preferably, the water-gas-shift process is conducted in one water-gas-shift reactor.

25 Preferably, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C.

Preferably, the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.



Preferably, no additional steam is added between the reforming processes and the water-gas-shift process.

Preferably, the water-gas-shift process comprises using a Cu-based catalyst.

5 Preferably, the method further comprises operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

Preferably, water is separated from the hydrogen-depleted shifted gas output from the hydrogen separation process.

10 Preferably, water is not separated from the shifted gas before the hydrogen separation process.

Preferably, the palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

Preferably, the carbon dioxide separation process is conducted cryogenically.

15 Preferably, the air separation unit is also arranged to generate nitrogen, and the method comprises generating ammonia in dependence on nitrogen output from the air separation unit and hydrogen output from the hydrogen separation process.

According to second aspect of the present invention, there is provided a hydrogen production plant arranged to perform the method of the first aspect.

20 According to third aspect of the present invention, there is provided an ammonia production plant arranged to perform the method of the first aspect.

## **BRIEF DESCRIPTION OF DRAWINGS**

25 Figure 1 shows a reforming process comprising a gas-heated reforming process and an autothermal reforming process.

Figure 2 shows a configuration of a hydrogen production process.

Figure 3 shows a configuration of a hydrogen production process according to an embodiment.

Figure 4 shows a configuration of a hydrogen production process according to an embodiment.

Figure 5 shows a configuration of a hydrogen production process according to an embodiment.

- 5 Figure 6 shows a configuration of a hydrogen production process according to an embodiment.

Figure 7 shows a configuration of a hydrogen production process according to an embodiment.

- 10 Figure 8 shows a configuration of a hydrogen production process according to an embodiment.

Figure 9 shows a configuration of a hydrogen production process according to an embodiment.

Figure 10 comprises Table 1.

Figure 11 comprises Table 2.

- 15 Figure 12 comprises Table 3.

Figure 13 comprises Table 4.

Figure 14 comprises Table 5.

Figure 15 comprises Table 6.

- 20 Figure 16 shows a configuration of an ammonia production process according to an embodiment.

## DETAILED DESCRIPTION OF EMBODIMENTS

A known method for the production of a CO<sub>2</sub>-rich gas stream and a H<sub>2</sub>-rich gas stream comprises the following steps:

- 25 a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas, also referred to as syngas, under supply of an O<sub>2</sub>-containing gas. Syngas mainly comprises H<sub>2</sub> and CO;

b) the gas stream from a) is shifted so as to produce a mixture of  $H_2$  and  $CO_2$  by reaction with  $H_2O$ ;

c)  $CO_2$  is separated from the gas stream from b) in a  $CO_2$  separation unit;

d)  $H_2$  is separated from the  $CO_2$ -depleted gas from c) in a  $H_2$  separation unit.

- 5 The above method describes the basic principles behind the production hydrogen from natural gas with separation of hydrogen and  $CO_2$ .

Known techniques combust the remaining gas after separation of  $CO_2$  and  $H_2$  as fuel. If a relatively high percentage of hydrogen has not been separated, then a significant amount of hydrogen will be wasted in this fuel. Furthermore, the combustion of any  
10 accompanying carbon containing species in the fuel produces uncaptured  $CO_2$ .

Most hydrogen producing processes from natural gas known in the art rely on the use of a steam reformer, and in some instances on an autothermal reformer (ATR), i.e. using an autothermal reactor, or a partial oxidation reactor. However, use of a gas-heated-reformer (GHR) in combination with an autothermal reformer is  
15 considerably more energy efficient.

Production and perspectives on syngas production has been described by J. R. Rostrup-Nielsen in *Catalysis Today*, volume 18, pages 305-324, 1993, and in volume 71, pages 243-247, 2002. There are several types of reformers for production of synthesis gas comprising steam reforming, autothermal reforming and partial  
20 oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled  
25 "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.

Separation of  $CO_2$  is frequently done by an amine washing process, and sometimes by using a physical sorbent like methanol.

Hydrogen is routinely separated from a hydrogen containing gas mixture by use of  
30 pressure swing absorption (PSA). Apart from being a large and costly part of the

hydrogen plant, PSA has the disadvantage of CO<sub>2</sub> being released at low pressure, e.g. atmospheric pressure, with the subsequent need for compression and cooling.

Embodiments provide new and particularly advantageous implementations of systems for producing hydrogen from natural gas. Hydrogen production may be the main purpose of the system. However, embodiments also include using at least some of the hydrogen to produce ammonia. Ammonia is an alternative energy carrier to compressed or liquefied hydrogen. In addition to the production of fertilizers, ammonia may be used as fuel in transportation, maritime and offshore markets.

In embodiments, the separation of the hydrogen from the syngas is performed particularly efficiently.

Embodiments also provide a high carbon capture efficiency that may be at least 90% of the carbon in the feed gas, and preferably at least 97%.

Although embodiments may separate CO<sub>2</sub> by using an amine washing process, embodiments preferably use cryogenic separation to separate CO<sub>2</sub>. That is to say, the gas stream is cooled to a temperature, and at a pressure, where CO<sub>2</sub> is liquefied.

Cryogenic separation of CO<sub>2</sub> has in the known art been assumed to be disadvantageous as a smaller fraction of CO<sub>2</sub> is separated. However, embodiments avoid this disadvantage by providing novel process design. CO<sub>2</sub> is obtained directly in a liquid form, i.e. ready for transportation to a deposition site.

Embodiments advantageously re-use the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> in the hydrogen production system. This improves the carbon capture efficiency of the system.

Embodiments advantageously use a palladium membrane (Pd-membrane) to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons. One advantage is that hydrogen is obtained with high purity; that may be greater than 99% and is often greater than 99.9%. Another advantage is that the gas containing CO<sub>2</sub> that does not pass through the membrane, which is referred to as the retentate, is at an elevated pressure, typically above 10 bar, more typically between 20 and 40 bar, but sometimes even at pressures up to 80 bar. It is even preferred that the Pd-membrane operates at an elevated

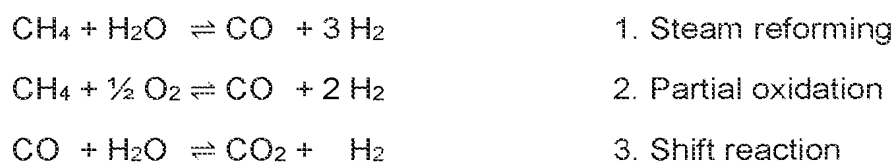
temperature; 200-400 °C, or in a narrower range above or around 300 °C, so that it is well suited for operation down-stream of the water-gas-shift (WGS) reactor or reactors.

Embodiments include receiving a supply of natural gas, or more generally a hydrocarbon containing gas from any source. The natural gas may be cleaned and pre-treated in a suitable manner so that the gas feed mainly comprises methane after treatment. Such cleaning typically comprises sulfur removal, for example by an ZnO absorber. The pre-treatment may also comprise a pre-reforming process whereby higher hydrocarbons, such as ethane, are converted by steam to methane and CO<sub>2</sub>.

- 5 The reforming process according to embodiments may take place at a pressure within the interval 10 to 200 bar.

The water-gas shift reaction according to embodiments may take place in a shift reactor. Steam may be supplied to the shift reactor, but the shift reactor may also be operated without supply of steam as steam already is introduced into the reformer. At the outlet of the shift reactor, the carbon content may comprise CO<sub>2</sub> and methane. CO<sub>2</sub> may be about 2% to about 5% by volume or higher. Methane may be about 2% to about 5% by volume or higher.

The following chemical reactions may take place during production of synthesis gas and hydrogen by reforming of natural gas:



- 20 The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by partial oxidation in an autothermal reformer.

In a steam reformer (SR) natural gas (i.e. methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer consists of many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space

- 25

demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer is approximately 950 °C. The energy which is used to carry out the

5 endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the produced stream is from 2.7 to 3.0. Synthesis gas produced from a steam reformer may contain approximately 3% methane by volume.

10 Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR, natural gas (methane) is fed together with oxygen or air into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the

15 combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions may be driven to equilibrium over a catalyst bed before the synthesis gas leaves the reactor at approximately 1000-1050 °C. The size of such a unit could be a height of 10-15 meters and a diameter of 5-6 meters. A typical ratio of steam:carbon in the output gas is from 0.6 to 1.4. The ratio of hydrogen to carbon

20 monoxide in the output gas is lower than 2. Typical methane slip, i.e. amount of unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR.

A further option for reforming natural gas is a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed.

25 The exit temperature for a POX is somewhat higher than for a typical ATR.

Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. In combined reforming,

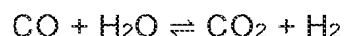
30 SR is operated at milder conditions (i.e. lower outlet temperature), which leads to a high methane slip. The residual methane is then reacted in the ATR. The ratio of

steam:carbon is in the area 1.8-2.4, with a ratio of hydrogen to carbon monoxide in the product gas higher than 2.

From the above, it is evident that the reformer unit has a very large footprint (SR), and that the exit gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB) that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting. It has been found, however, that a more efficient process is experienced if the hot output gas is used to reform part of the natural gas before it enters the autothermal reformer. This combination of ATR with oxygen and a gas-heated-reformer (GHR) has been tested in a demonstration unit for production of methanol. This development originates in ICI in the 1980s to completely remove the traditional steam reformer in their Leading Concept Methanol (LCM) process.

Figure 1 shows an efficient reforming process that may be used in embodiments. The hot exit gas from the reformer is used to reform part of the natural gas before it enters the autothermal reformer. Instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR 1, then the partially reformed gas in stream 21 passes through the ATR 2, and finally the reformed gas in stream 22 passes through the heating side of the GHR 1 to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only moderate further cooling before the water-gas-shift process (WGS).

After reforming of the natural gas and cooling, the gas mixture is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and some CH<sub>4</sub>. Between these components there is an equilibrium relation given by the stoichiometric equation:



This reaction is called the water-gas-shift (WGS) reaction, and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors may be used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. The catalyst in the first step may be based on chromium/iron, whereas the catalyst in the second step may be a copper/zinc catalyst. In the shift unit CO and H<sub>2</sub>O are reacted to form CO<sub>2</sub> and H<sub>2</sub>, and in known techniques it is often a requirement that the mentioned reaction is driven to the right to the highest possible degree, so that as little CO as possible is present in the gas mixture exiting the shift unit. A low content of CO in the mentioned gas mixture again gives a high purity of the H<sub>2</sub>-rich gas stream out of the separation unit.

In known techniques the shift reactor is operated so that the ratio H<sub>2</sub>O:CO to the shift reactor is high, e.g. equal to 10:1, so that there is a high conversion of CO.

Embodiments may differ from such techniques by optimizing the processes in a WGS reactor in conjunction with a hydrogen separation processes by a palladium membrane. The efficiency of a Pd membrane may be improved by operating at a certain elevated temperature. Preferably, only a high-temperature WGS is therefore applied before the membrane. A low-temperature WGS may also be used after the membrane and the shifted gas partly recycled, i.e. fed back into one of the earlier processes in the hydrogen production process.

In a preferred embodiment, the temperature of the WGS process is determined in dependence on an operating condition of the Pd-membrane. For example, the temperature of the WGS process may be set substantially at the operating condition of the Pd-membrane, e.g. about 300 °C, thereby avoiding any need for heat



exchange between the two units. It is not necessary for the WGS process to be operated in a way that maximizes the conversion of CO because the rest gas is recycled back into the earlier processes. Embodiments include no additional steam being added before the WGS reactor. When the Pd-membrane is operated at about  
5 300 °C, a Cu-based catalyst may be used.

Gases in the mixture after the shift reactor, or the shift reactors, can be separated more or less completely based on the different properties of the gas molecules. The most common techniques are absorption, adsorption and cryogenic distillation.

CO<sub>2</sub> is an acid gas, and the most widely used method to separate the mentioned gas  
10 from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by altering the composition of the liquid or by altering pressure and temperature. For  
15 separation of CO<sub>2</sub>, aqueous solutions of alcoholamines can be used. The absorption takes place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO<sub>2</sub> from the amine phase in the stripping unit, stripping steam is usually used. If the partial pressure of CO<sub>2</sub> in the gas into the absorber is high, e.g. higher  
20 than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO<sub>2</sub> can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar. Other absorption technologies rely on alternative physical liquid absorbents like methanol at reduced temperature.

Embodiments preferably separate hydrogen from the gas output from the WGS  
25 reactor using a membrane. In particular, a Pd-film membrane may be used. By the use of one or more semipermeable or dense membrane units, molecules of different size and different properties can be made to permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture from the WGS reactor, membranes can be selected where H<sub>2</sub> permeates rapidly, whereas  
30 CO<sub>2</sub> permeates slowly or not at all, so that separation of the different gas components is achieved. The membrane may be a palladium membrane.

The driving force over the membrane is the difference in partial pressure, i.e. of hydrogen between the process gas (which is the received gas on the retentate side of the membrane) and gas on the permeate side of the membrane. As hydrogen in many cases is required at an elevated pressure, a way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. Although embodiments include using a sweep gas, this is optional and embodiments also include not using a sweep gas.

Embodiments may alternatively use a combination of solid membranes and liquid membranes through which there is a rapid permeation of  $\text{CO}_2$ , while  $\text{H}_2$  is kept back.

A known gas separation technique is pressure-swing adsorption (PSA). PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material. In the present mixture of gases,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  are adsorbed, letting the hydrogen pass through at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit. Alternatively, the temperature can swing instead of the pressure.

Capturing  $\text{CO}_2$  by refrigeration is a cost and energy efficient method compared to other technologies. In known techniques, electricity may be used to drive the compressors. The main challenge has been that only in the order of 90% of  $\text{CO}_2$  is captured this way, or perhaps 93% by optimizing conditions. In addition, there are some carbon losses from unconverted  $\text{CO}$  and  $\text{CH}_4$  and these reduce the overall carbon capture to 90% or below.

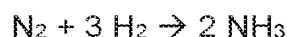
Embodiments include separating out  $\text{CO}_2$  and then depositing the separated  $\text{CO}_2$ . Large amounts of  $\text{CO}_2$  can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced

oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO<sub>2</sub> gas has to be brought to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO<sub>2</sub> gas  
 5 can be separated from the H<sub>2</sub>/CO<sub>2</sub> mixture at an elevated pressure, significant compression work can be avoided.

Embodiments may allow a selection to be made between collecting hydrogen and CO<sub>2</sub> at the high (process) pressure. A hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen, is needed for storage and in  
 10 transportation applications. As it is more demanding to pressurize hydrogen than CO<sub>2</sub>, separation technologies that provide hydrogen at high pressure are sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen-permeable membrane.

Embodiments include using an air separation unit (ASU) to generate oxygen. The  
 15 oxygen may be supplied to an autothermal reactor, ATR, used in the reforming process. The ASU may cryogenically separate air into oxygen and a gas mixture that mostly comprises nitrogen. Embodiments include using the nitrogen, from the ASU, and hydrogen, from the membrane separator, to generate ammonia.

Combining nitrogen with hydrogen allows production of ammonia, NH<sub>3</sub>, according to  
 20 the reaction:

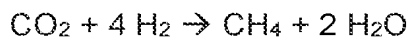


Ammonia can be used as an environmentally friendly fuel as long as any CO<sub>2</sub> generated during production is captured. The benefits of using ammonia include ease of transportation and handling. Liquid ammonia can be stored in vessels at  
 25 about 17 bar.

The ammonia process is favored by high pressures, and an elevated temperature is needed for sufficient reaction rate.

A known production technique of ammonia is from natural gas, or sometimes from higher hydrocarbons, by reforming the gas to syngas that is shifted to mostly

hydrogen and CO<sub>2</sub>. Using air in the process stream, like applying an ASU, gives a mixture of hydrogen, nitrogen, water and CO<sub>2</sub> after shift conversion. The shift reaction is frequently carried out in two steps, high-temperature and low-temperature shift, to convert CO to low levels. Before the ammonia synthesis, water is knocked out and CO<sub>2</sub> removed by elaborate means. Further, residual CO and CO<sub>2</sub> has to be removed as they are poisons for the catalyst, and this is done by methanation;



The ammonia synthesis loop is also known as Haber-Bosch synthesis. The reaction is run over a catalyst that typically is promoted magnetite. Single pass conversion over the catalyst is around or below 20% and, therefore, significant recycle is required. The pressure is in the range 60-200 bar depending on process design. This is significantly higher than reforming and shifting natural gas that takes place in the pressure range 20-35 bar. On the other hand, the reaction pressure to make ammonia is significantly lower than the 300-700 bar required for hydrogen as energy carrier. Reaction temperature is ca. 450 °C. There have been many types of design of ammonia plants during the last 60 years. One option that has been explored is to produce hydrogen from steam reforming combined with PSA, and combined this hydrogen with nitrogen from an ASU-unit. Such a plant, however, is not favorably designed for separating a pure CO<sub>2</sub>-stream for storage.

Embodiments are described in more detail by the following examples of embodiments and figures.

Process simulations using the program UniSim are based on natural gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher hydrocarbons, 1.5% CO<sub>2</sub> and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. The natural gas flow is 4625 kg/h; 246 kmol/h. Hydrogen specification is > 99.97 mol% for fuel cells, and specification for CO<sub>2</sub> is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C.

A total of 5 process schemes are analyzed. These are one comparative example and four implementations of embodiments, as summarized in Table 1 in Figure 10.

The schemes vary in WGS temperature, use of Pd-membrane or PSA for hydrogen separation, use of amine solvents or cryogenic CO<sub>2</sub> separation, as well as the position of water condensation.

The membrane may be always operated at a preferable temperature for permeation of hydrogen through the membrane. For example, the membrane may be operated at 300 °C. However, the WGS may be operated at 256 °C for highest CO conversion, but at 300 °C when the shifted gas is directly introduced to the membrane; i.e. without any heat exchange and water condensation.

The conditions of Embodiment Example 2 are applied in Embodiment Examples 5-7, where recycle of rest gas is used.

The following reasonable assumptions are made, but without fixing these conditions: in amine cases, it is assumed that 100% of inlet CO<sub>2</sub> is removed by the unit; in membrane cases, 93% H<sub>2</sub> separation is assumed; produced H<sub>2</sub> from the membrane unit is at 3 bar and compressed to 350 bar for export; the final CO<sub>2</sub> stream is delivered at -26.2 °C at 16 bar. It is understood that the applied conditions are reasonable for comparing different process schemes, but that a variety of other conditions can be used; e.g. for different natural gas compositions, requirements for delivery of hydrogen and CO<sub>2</sub>, and site specific conditions like possibilities for integration with other process units and the availability of electricity from the grid.

## Comparative Example

Figure 2 is a process flow sheet showing production of hydrogen and CO<sub>2</sub> by combination of ATR 2 and GHR 1 according to a comparative example to embodiments.

The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen stream 101 is optionally added to the pretreated natural gas 41 as stream 103 and fed to the optional pre-reformer 4. The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen 51 from an air separation unit (ASU) 5 is added to the ATR 2. The ASU separates cryogenically air 53 into oxygen 51 and

nitrogen 52, sometimes also producing noble gases like argon. It should be understood that embodiments include any other means for producing oxygen, or air enriched in oxygen, such as by using vacuum or pressure swing adsorption, or by using a membrane.

- 5 The produced syngas 12 is shifted to increase the content of hydrogen and CO<sub>2</sub> in one or more shift reactors 6, i.e. water-gas-shift reactor(s) 6, to produce the shifted gas 61. Steam may be added to the gas mixture before the gas mixture is input into the shift reactor(s) 6. The addition of steam increases the efficiency of the shift reaction. The shifted gas 61 is subsequently cooled in the condenser 7 to remove its
- 10 water content 72, thus obtaining dry shifted syngas 71. Amine type separation process 8 separates CO<sub>2</sub> 81 from the shifted gas, and the CO<sub>2</sub> 81 is then compressed 9 and liquefied. The produced CO<sub>2</sub> 91 may be stored at site, shipped for permanent storage or directly injected into a geological formation for storage. Hydrogen 101 is separated in the process 10 by the known technique of pressure-
- 15 swing adsorption (PSA), that separates the hydrogen from the gas 82 that has already been depleted of CO<sub>2</sub> by the process 8. The separate outputs from the process 10 are hydrogen 101 and a rest-gas 102. The rest-gas 102 contains remnants of CO and CH<sub>4</sub> together with unseparated CO<sub>2</sub> and hydrogen. The energy in the rest gas is utilized for fuel in fired heater(s) for preheating of feed gases natural
- 20 gas and water/steam. Finally, the produced hydrogen 101 is compressed 11 to give hydrogen 111 at 340 bar.

The simulations show that production of 100 kNm<sup>3</sup>/hr hydrogen requires 35.7 kNm<sup>3</sup>/hr of NG and 16.7 kNm<sup>3</sup>/hr of oxygen. 622 tons of CO<sub>2</sub> is captured each year, assuming that the PSA rest-gas 102 is used for combustion and the exhaust gas CO<sub>2</sub>

25 emitted to the atmosphere. This gives a CO<sub>2</sub> capture efficiency of 95.4%. Electric power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

### **Embodiment example 1**

- 30 Figure 3 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 1. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming

4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

The present embodiment differs from the above-provided comparative example in that hydrogen separation is performed before CO<sub>2</sub> separation. After the WGS process, the shifted gas enters a hydrogen separation vessel that comprises a Pd-membrane 12. The hydrogen separation vessel may receive the output gas from the WGS reactor on the retentate side of the Pd-membrane. Hydrogen passes through the Pd-membrane to reach a permeate side of the Pd-membrane. The hydrogen on the permeate side of the Pd-membrane is output as stream 121. The gas stream output from the retentate side of the Pd-membrane is hydrogen-depleted gas 122.

The hydrogen stream 121 is sent to compressor 11 while the hydrogen-depleted gas stream 122 is depleted of water 72 in the condenser 7. The dried gas 73 is then input into the amine separator 8 that outputs CO<sub>2</sub> stream 81 and a rest-gas 83. CO<sub>2</sub> stream 81 is compressed 9, and the CO<sub>2</sub> depleted rest-gas 83 may be used for providing energy in fired heater(s).

Advantageously, the use of a Pd-membrane separator for separating hydrogen as the subsequent process to the WGS process allows the hydrogen separation process to be performed particularly efficiently and effectively. In particular, the temperature and/or pressure conditions in the WGS reactor may be selected in order to substantially optimize the operating conditions of the membrane separator (e.g. to maximize the separation of hydrogen in the membrane separator).

## Embodiment example 2

Figure 4 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 2. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of

hydrogen by Pd-membrane and water condensation 7 may be as described with reference to Figure 3 with corresponding reference signs.

A difference between embodiment example 2 and embodiment example 1 is that the amine unit 8 of embodiment example 1 is replaced with cryogenic separation 13 of CO<sub>2</sub> 131 from the dried gas 73, giving the rest-gas 132 for use in fired heater(s).

### **Embodiment example 3**

Figure 5 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 3. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. This embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as stream 71. In addition, reducing the water concentration before the membrane unit may advantageously increase the hydrogen concentration and may protect materials in the membrane unit.

The use of water condenser 7 on the gas output from the retentate side of the membrane separator 12 is optional.

CO<sub>2</sub> 81 is removed in an amine unit 8 leaving an energy rich rest-gas 84.

### **Embodiment example 4**

Figure 6 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 4. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.



The present embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such a configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as stream 71.

- 5 CO<sub>2</sub> 131 is removed in the cryogenic unit 13 leaving an energy rich rest-gas 132.

A comparison of the comparative example and embodiment examples 1-4 is provided below.

- A comparison of performance of the comparative example and embodiment examples 1, 2, 3 and 4 is listed in Table 2 in Figure 11. There are, in addition, differences in investment and operating costs (i.e. CAPEX and OPEX). As to the investment costs, prices from vendors show that for hydrogen separation, PSA is considerably more costly than using a Pd-membrane, and that for CO<sub>2</sub> separation, using amine is significantly more costly than cryogenic separation. In addition, the footprints of PSA and amine are much larger than for Pd-membrane and cryogenic CO<sub>2</sub> separation.

- Using a Pd-membrane, as in embodiment examples 1-4, is advantageous due to lower cost, smaller footprint and a higher hydrogen recovery factor than the comparative example. Note from the H<sub>2</sub> recovery factor that only 7% of the hydrogen in the shifted gas is lost in embodiment examples 1-4, compared to 14% in the comparative example. The percentage of carbon captured is above the 95% mark for embodiment examples 1 and 3, which is fully acceptable for most projects, although these still use amine separation of CO<sub>2</sub>. The amine separation in these two embodiments is, however, significantly simpler than in the comparative example, due to the more than 3-fold higher concentration of CO<sub>2</sub> in the inlet gas. Other factors to be considered are the conversion in the WGS (see Table 2 in Figure 11), and differences in how water is condensed (see Table 1 in Figure 10 as well as the figures).

- Known techniques are based on the assumption that a high conversion of CO in the WGS reactor results in better system performance with regard to hydrogen and CO<sub>2</sub> recovery. However, test of embodiments show that the performance of the

separation technologies is more dominant on the overall system performance. Accordingly, operating the WGS at 300 °C is advantageous.

There is no condensation of water and heat exchange after WGS and before the Pd-membrane in Embodiment Examples 1 and 2, in contrast to Embodiment Examples 3 and 4. The discussed advantages are summarized in Table 3 in Figure 12. It follows that using a Pd-membrane is preferable compared the comparative example, and that there is no need to adjust temperature and knock out water directly after WGS.

### **Embodiment examples 5-7**

Figure 7 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment Examples 5-7.

The processes in embodiment Examples 5-7 may be substantially the same, or identical, to Embodiment Example 2 except that the rest-gas 132 is recycled to the ATR 2.

The oxygen feed 51 may be adjusted to secure a constant exit temperature from ATR of about 1020 °C. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. The separation of hydrogen by a Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation 13 may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest-gas 132 is used as recycle-gas to the ATR 2. The processes in the ATR 2 are therefore adapted so that the rest-gas can additionally be received by the ATR 2.

The difference between Embodiment Examples 5-7 is in the amount of rest gas that is recycled, which is detailed in Table 4 in Figure 13.

### Comparison of Embodiment Examples 2 and 5-7

In Table 4 in Figure 13, Embodiment Examples 5-7, with recycle of rest gas, are compared to Embodiment Example 2. Although Embodiment Example 2 shows good performance, as seen in Table 3 in Figure 12, it is desirable to improve the efficiency of CO<sub>2</sub> capture and the carbon capture fraction. Embodiments achieve this by recycling at least part of the rest-gas to the reformer section. The results outlined in Table 4, in Figure 13, show a surprising effect in that much better performances are reached. Hydrogen production increases, with a recovery of 99% for Embodiment Example 7 (90% recycle), compared to 93% H<sub>2</sub> recovery for Embodiment Example 2 as defined in Table 2 in Figure 11; a hydrogen loss is reduced from 7% to 1%. Simultaneously, the carbon capture increases from 90% in Embodiment Example 2 to 99% in Embodiment Example 7, the best performance of all examples.

When the production and separation efficiencies increase, more oxygen is needed in the ATR and less fuel gas is available for heat generation. The advantages summarized in Table 5, in Figure 14, indicates that a high degree of recycle is preferable. Probably more important is that a superior carbon capture fraction, as in Embodiment Example 7, is considered a decisive advantage in many hydrogen projects.

### Embodiment Example 8

Figure 8 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 8 which may be identical to Embodiment Example 2 except that the rest-gas 133 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the WGS 6. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest-gas 133 is used as recycle-gas to the WGS 6. Process simulations have

been made for recycle of 50%, 80% and 90% of rest-gas to WGS. However, embodiments include using any feasible recycle ratio of the rest gas.

### **Embodiment Example 9**

Figure 9 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 9 which may be identical to Embodiment Example 2 except that the rest-gas 134 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the membrane unit 12. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by the Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest-gas 134 is used as recycle-gas to the membrane unit 12. Process simulations have been made for recycle of 50%, 80% and 90% of rest-gas to the Pd-membrane. However, embodiments include using any feasible recycle ratio of the rest gas.

### **Embodiment Example 10**

Embodiment Example 10 is identical to Embodiment Examples 5-7 except that the oxygen feed 51 is kept constant compared to Embodiment Example 2. This reduces the exit temperature from the ATR 2 from 1020 °C to, respectively, 1008 °C, 999 °C, 989 °C and 974 °C for 30%, 50%, 80% and 90% recycle.

### **Comparison of Embodiment Examples 2, 6, 8, 9 and 10**

Table 6, in Figure 15, summarizes 80% recycle of rest-gas from CO<sub>2</sub> separation compared to no recycle. The recycle is to the ATR, WGS and Pd-membrane respectively. For recycle to ATR, the oxygen feed has been increased in Embodiment Example 6 to keep the exit temperature constant. The following surprising advantageous effects are found:

- Hydrogen production increases significantly for all recycle cases.

- Carbon capture rate increases significantly for all recycle cases.
- Very high capture rates are obtained when recycle is to ATR or WGS.
- Recycle to ATR without increasing oxygen flow is beneficial.
- More energy for fired heater is available when recycle is to Pd-membrane.

## 5 Embodiment Example 11

Figure 16 shows a system according to Embodiment Example 11.

Embodiment Example 11 is directed towards producing ammonia 141 and is similar to all previous Embodiment Examples in that a Pd-membrane 12 is used to separate hydrogen, the syngas is produced by a combination of GHR 1 and ATR 2, and there is a WGS reactor(s) 6.

In the present embodiment, nitrogen 52, from the ASU 5, is combined with hydrogen, from the membrane separator 12, in an ammonia synthesis unit 14. The hydrogen supplied to the ammonia synthesis unit 14 may be either hydrogen stream 121 or the compressed hydrogen stream 111.

A preferred implementation of the present embodiment is shown in Figure 16. This is similar to Embodiment Example 8 and has corresponding reference signs. However, embodiments also include alternatively generating the hydrogen supply using any of the other Embodiment Examples described herein, and using any recycle ratios of rest gas.

Advantages of using systems according to the present embodiment for the production of ammonia include, but are not limited to, efficient natural gas reforming by using GHR/ASU, one-step WGS reaction, hydrogen separation at the same temperature as WGS, ease of separating CO<sub>2</sub> by cryogenic cooling, high hydrogen productivity and low CO<sub>2</sub> emission by recycle of rest gas, and low content of inerts in the ammonia synthesis loop.

The embodiments presented throughout the present document provide advantageous methods and systems for the production of hydrogen and/or ammonia. In particular, the use of a Pd-membrane to separate hydrogen immediately downstream of a WGS reactor has a surprising synergistic effect. Contrary to known techniques, the WGS reactor may be operated at substantially the same temperature

as the Pd-membrane. The WGS reactor may be operated under conditions that are more preferable for the effective operation of the Pd-membrane and this can substantially improve the overall efficiencies and effectiveness of the system.

In a particularly preferred implementation according to an embodiment, the hydrogen separation process uses a hydrogen separation device as disclosed in the published patent application WO2020/012018A1, the entire contents of which are incorporated herein by reference. The hydrogen separation device disclosed in WO2020/012018A1 uses Pd-membranes to separate hydrogen from a gas mixture. The operational capabilities of the hydrogen separation device disclosed in WO2020/012018A1 result in it being particularly suitable for use in the hydrogen and/or ammonia production processes according to embodiments.

Other particularly advantageous techniques that may be used in methods and systems according to embodiments are the recycling of the rest gas directly to the Pd-membrane separator and/or water gas shift (WGS) reactor.

Embodiments include a number of modifications and variations to the above described techniques.

Embodiments use a Pd-membrane separator 12 to separate hydrogen from shifted gas. Optionally, a sweep gas may be used on the permeate side of the membrane. The sweep gas may be steam. The steam may be at an elevated total pressure above 5 bar, preferably above 10 bar.

Embodiments include the use of a water separator, such as a condenser, in between the Pd-membrane separator 12 and the hydrogen compressor 11 to separate hydrogen from the used sweep gas.

Embodiments also include optionally using a sweep gas on the retentate side of the membrane.

In embodiments, a) sulfur may be removed from the feed gas, b) the feed gas may be saturated with water, c) hydrogen may optionally be added to the gas stream before pre-reforming the gas that has been subject to treatments a and b, d) the gas from c may be reformed by a combination of gas-heated reforming and autothermal reforming, e) the reformed gas may be subjected to water-gas-shift to give a shifted gas, f) hydrogen may be separated from the shifted gas using a Pd-membrane, g)

carbon dioxide may be separated from the shifted gas that has been subject to treatment f, h) the separated hydrogen is optionally compressed and liquefied, i) the separated carbon dioxide is optionally compressed and liquefied.

5 In embodiments, at least part of the rest gas from separating hydrogen and carbon dioxide may be recycled.

In embodiments, the portion of the rest gas that is recycled may be more than 50%, preferably around 80%, more preferably at least 90%. Embodiments include all of the rest being recycled.

10 In embodiments, the rest gas that is recycled may be fed back into the gas-heated reforming process.

In embodiments, the rest gas that is recycled may be fed back into the autothermal reformer, the water-gas-shift reactor(s) and/or the Pd-membrane.

In embodiments, the feed gas may be natural gas.

15 In embodiments, the feed gas may be a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.

In embodiments, the gas-heated reformer may be heated by the exit gas from an autothermal reformer.

20 In embodiments, the exit temperature of the reformed gas from the gas-heated reformer may be in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

In embodiments, the autothermal reformer may be supplied with oxygen from an air separation unit.

In embodiments, the autothermal reformer may be supplied with oxygen or oxygen enriched air from a membrane air separation unit.

25 In embodiments, the water-gas-shift reaction may be conducted in a high-temperature-shift and a low-temperature shift reactor.

In embodiments, the water-gas-shift reaction may be conducted in one reactor.

In embodiments, the water-gas shift reactor may be operated at a temperature between 200 and 300 °C, preferably between 240 and 270 °C.

In embodiments, the water-gas shift reactor may be operated at a temperature between 270 and 330 °C, preferably between 290 and 310 °C, most preferably at about 300 °C.

5 In embodiments, no additional steam may be added between the reformer and the WGS-reactor.

In embodiments, the water-gas shift reactor may utilize a Cu-based catalyst.

In embodiments, the CO conversion in the WGS reactor may be at least 90%, but below 98%, more preferably below 96%.

10 In embodiments, hydrogen may be separated before CO<sub>2</sub> is separated from the shifted gas.

In embodiments, the WGS and the Pd-membrane may be operated at about the same temperature.

In embodiments, water may be separated after the Pd-membrane and not before the membrane.

15 In embodiments, the Pd-membrane may be operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

In embodiments, carbon dioxide may be separated cryogenically. The carbon dioxide may be deposited in a geological reservoir.

20 In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by a nearby processing plant.

In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by electricity from the grid and/or electricity from renewable energy source(s).

25 In embodiments, nitrogen may be produced by the air separation unit.

In embodiments, nitrogen and hydrogen may be used to produce ammonia. In embodiments, methanisation may be substantially avoided in the ammonia synthesis.

The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather,



the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed

5    embodiments without departing from the spirit and scope of the invention as set forth in the appended claims.

**Claims:**

1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide, wherein

the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process, and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process to thereby generate hydrogen and a hydrogen-depleted shifted gas; and

performing a carbon dioxide separation process on the hydrogen-depleted shifted gas to thereby generate carbon dioxide;

wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a palladium membrane, wherein the hydrogen separator comprises a permeate side of the palladium membrane and a retentate side of the palladium membrane, and the shifted gas is input to the retentate side of the palladium membrane;

outputting hydrogen from the permeate side of the palladium membrane; and

outputting hydrogen-depleted shifted gas from the retentate side of the palladium membrane.

- 5        2. The method according to claim 1, further comprising performing a sulfur removal process on the feed gas before performing the reforming processes on the feed gas.
- 10       3. The method according to claim 1 or 2, further comprising performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; and
- the method further comprising:
- 15       optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and
- optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.
- 20       4. The method according to any of the preceding claims, wherein the carbon dioxide separation process generates carbon dioxide and a rest gas, and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one of said performed processes in the
- 25       method of producing hydrogen.
5. The method according to claim 4, wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.
- 30       6. The method according to claim 4 or 5, wherein the rest gas that is recycled is fed back into the autothermal reforming process.
- 35       7. The method according to claim 4 or 5, wherein the rest gas that is recycled is fed back into the water-gas-shift process.

8. The method according to claim 4 or 5, wherein the rest gas that is recycled is fed back into the hydrogen separation process.

9. The method according to any of the preceding claims, wherein the feed gas is natural gas.

10. The method according to any of the preceding claims, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.

11. The method according to any of the preceding claims, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

12. The method according to any of the preceding claims, wherein the autothermal reforming process is supplied with oxygen from an air separation unit.

13. The method according to any preceding claim, wherein the water-gas-shift process is conducted in one water-gas-shift reactor.

14. The method according to claim 13, wherein the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C.

15. The method according to any of the preceding claims, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

16. The method according to any of the preceding claims, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

17. The method according to any of the preceding claims, wherein the water-gas-shift process comprises using a Cu-based catalyst.
- 5 18. The method according to any of the preceding claims, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.
- 10 19. The method according to any of the preceding claims, wherein water is separated from the hydrogen-depleted shifted gas output from the hydrogen separation process.
20. The method according to any of the preceding claims, wherein water is not separated from the shifted gas before the hydrogen separation process.
- 15 21. The method according to any of the preceding claims, wherein the palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.
- 20 22. The method according to any of the preceding claims, wherein the carbon dioxide separation process is conducted cryogenically.
- 25 23. The method according to claim 12, or any claim dependent thereon, wherein the air separation unit is also arranged to generate nitrogen, and the method comprises generating ammonia in dependence on nitrogen output from the air separation unit and hydrogen output from the hydrogen separation process.
24. A hydrogen production plant arranged to perform the method of any of claims 1 to 22.
- 30 25. An ammonia production plant arranged to perform the method of claim 23.

**Abstract**

Disclosed herein is a method of producing hydrogen, the method comprising:

5 receiving a feed gas comprising hydrocarbons; performing reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide, wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process, and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

10 performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process to thereby generate hydrogen and a hydrogen-depleted shifted gas; and performing a carbon dioxide separation process on the hydrogen-depleted shifted gas to thereby generate carbon dioxide; wherein the hydrogen separation process

15 comprises: inputting the shifted gas to a hydrogen separator that comprises a palladium membrane, wherein the hydrogen separator comprises a permeate side of the palladium membrane and a retentate side of the palladium membrane, and the shifted gas is input to the retentate side of the palladium membrane; outputting hydrogen from the permeate side of the palladium membrane; and outputting

20 hydrogen-depleted shifted gas from the retentate side of the palladium membrane.

[Fig. 9]

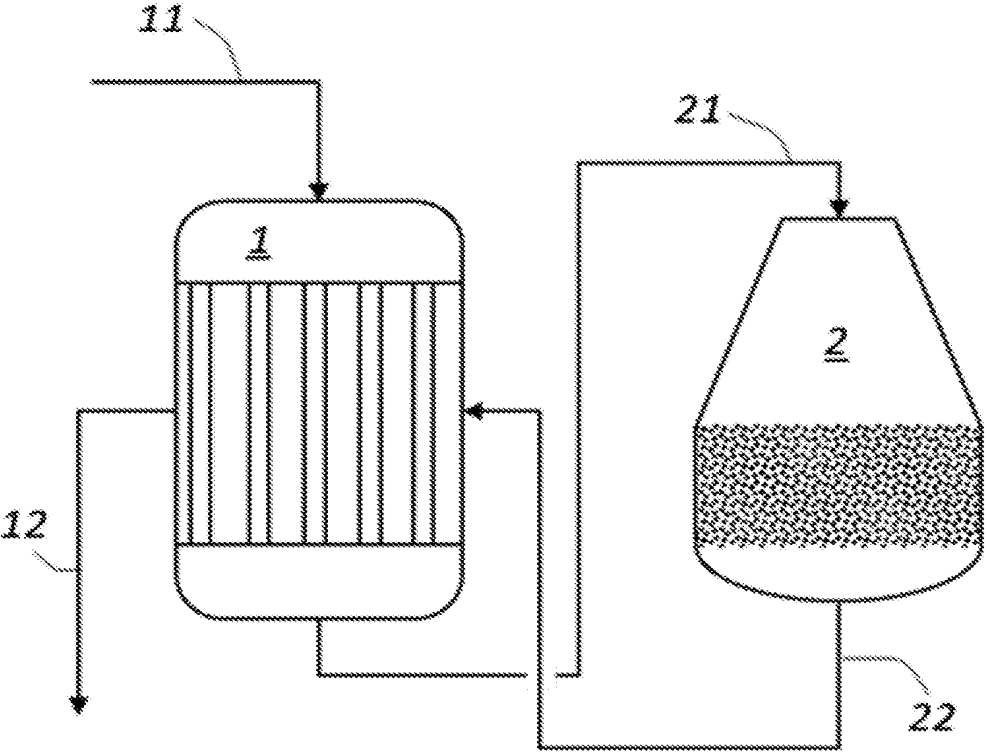


FIGURE 1

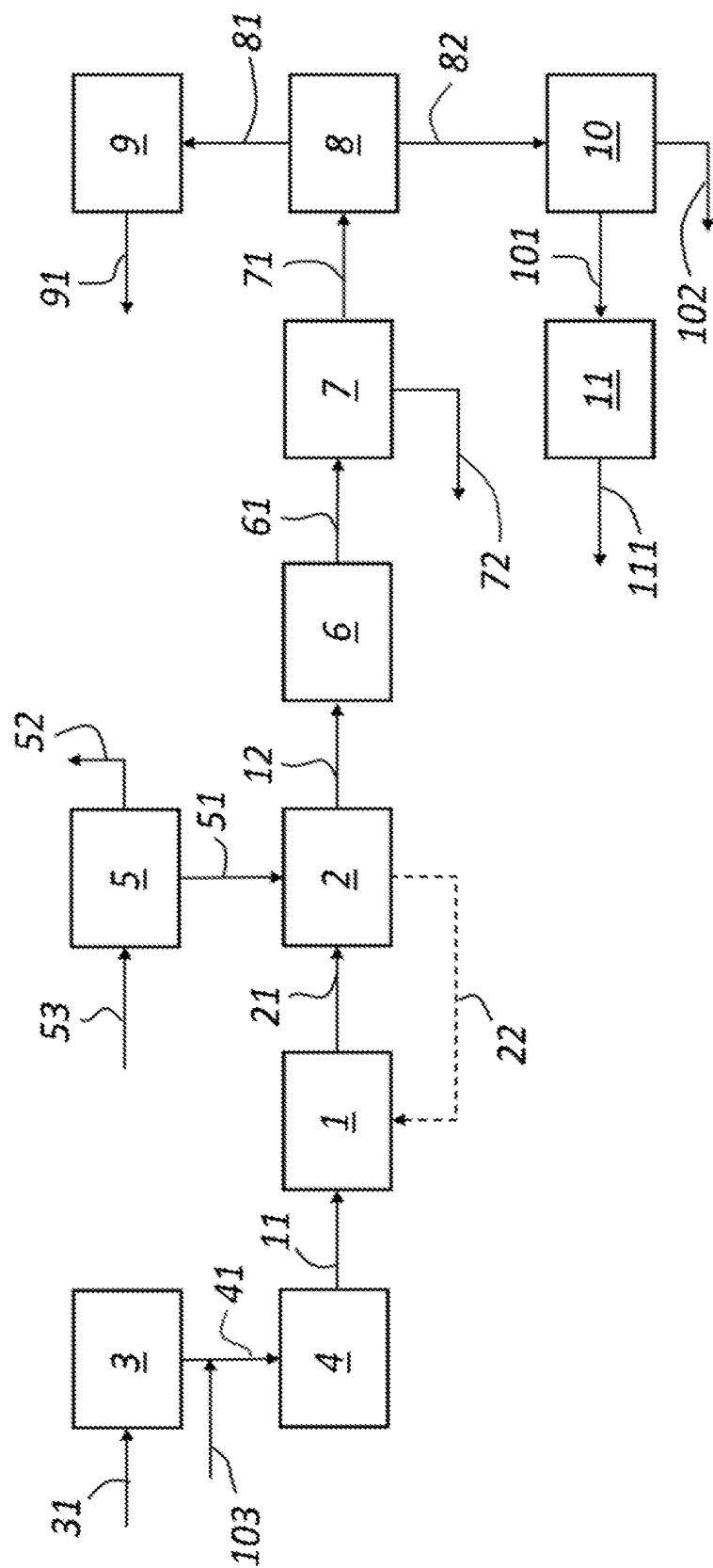


FIGURE 2



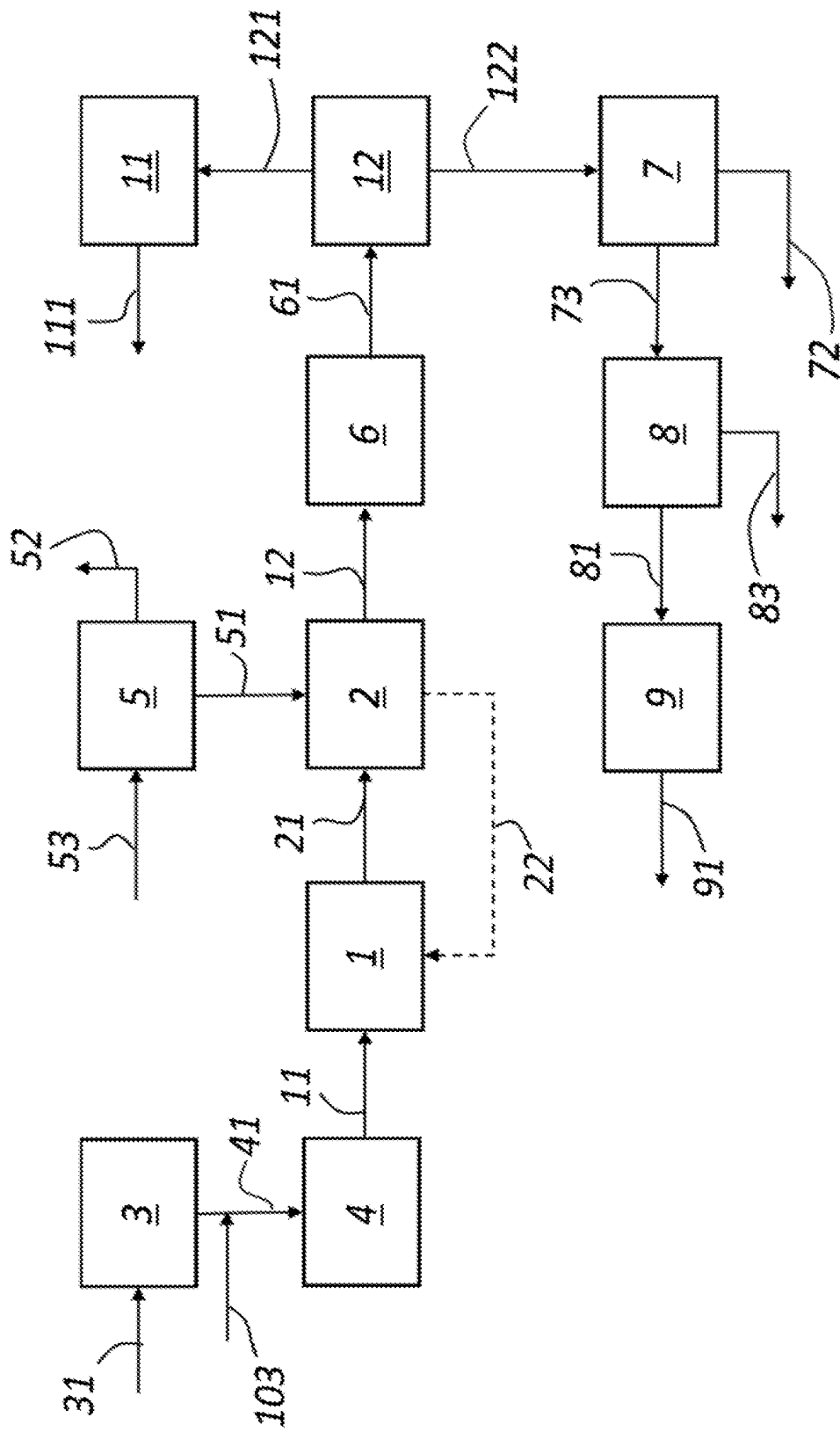


FIGURE 3

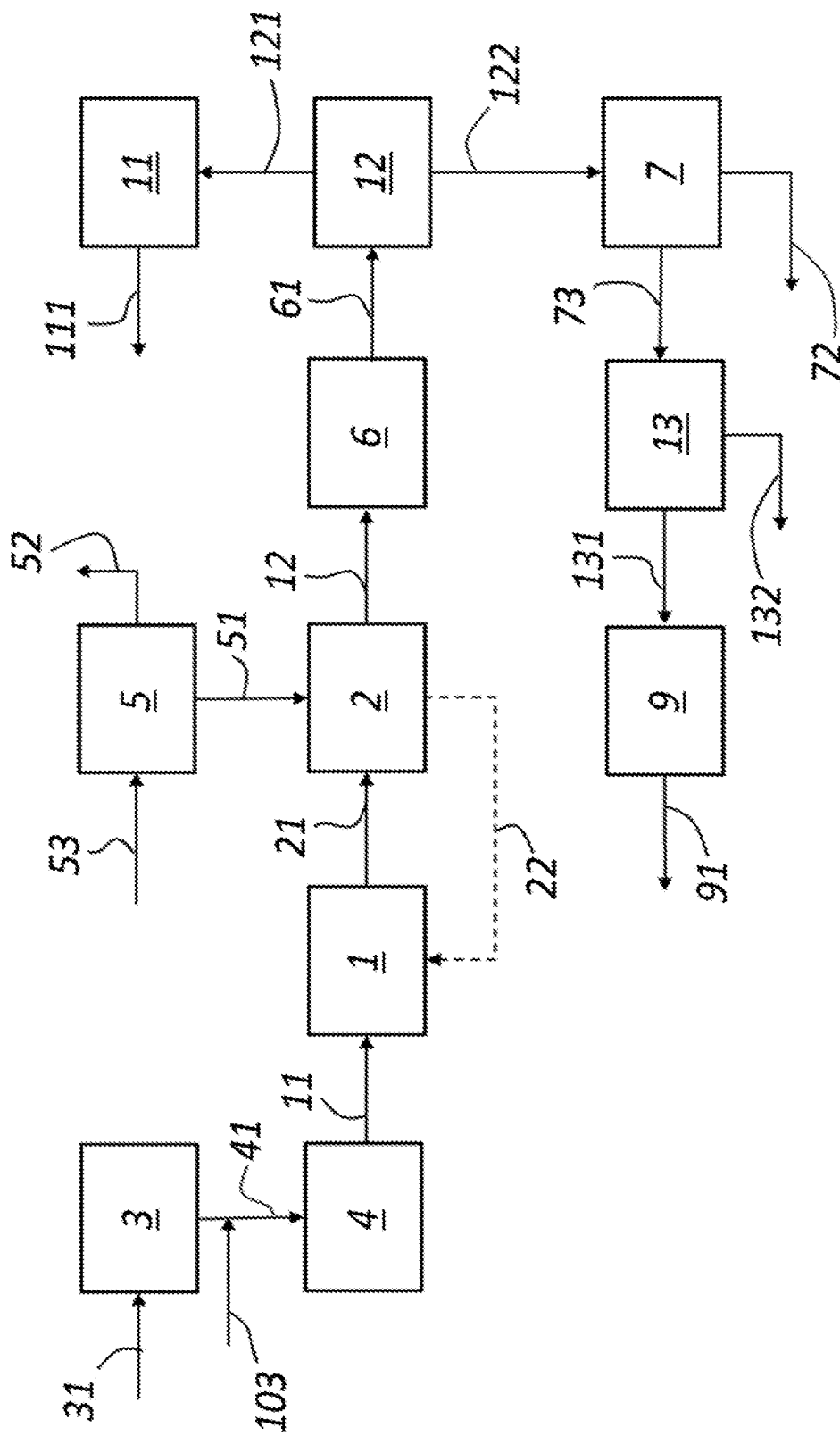


FIGURE 4

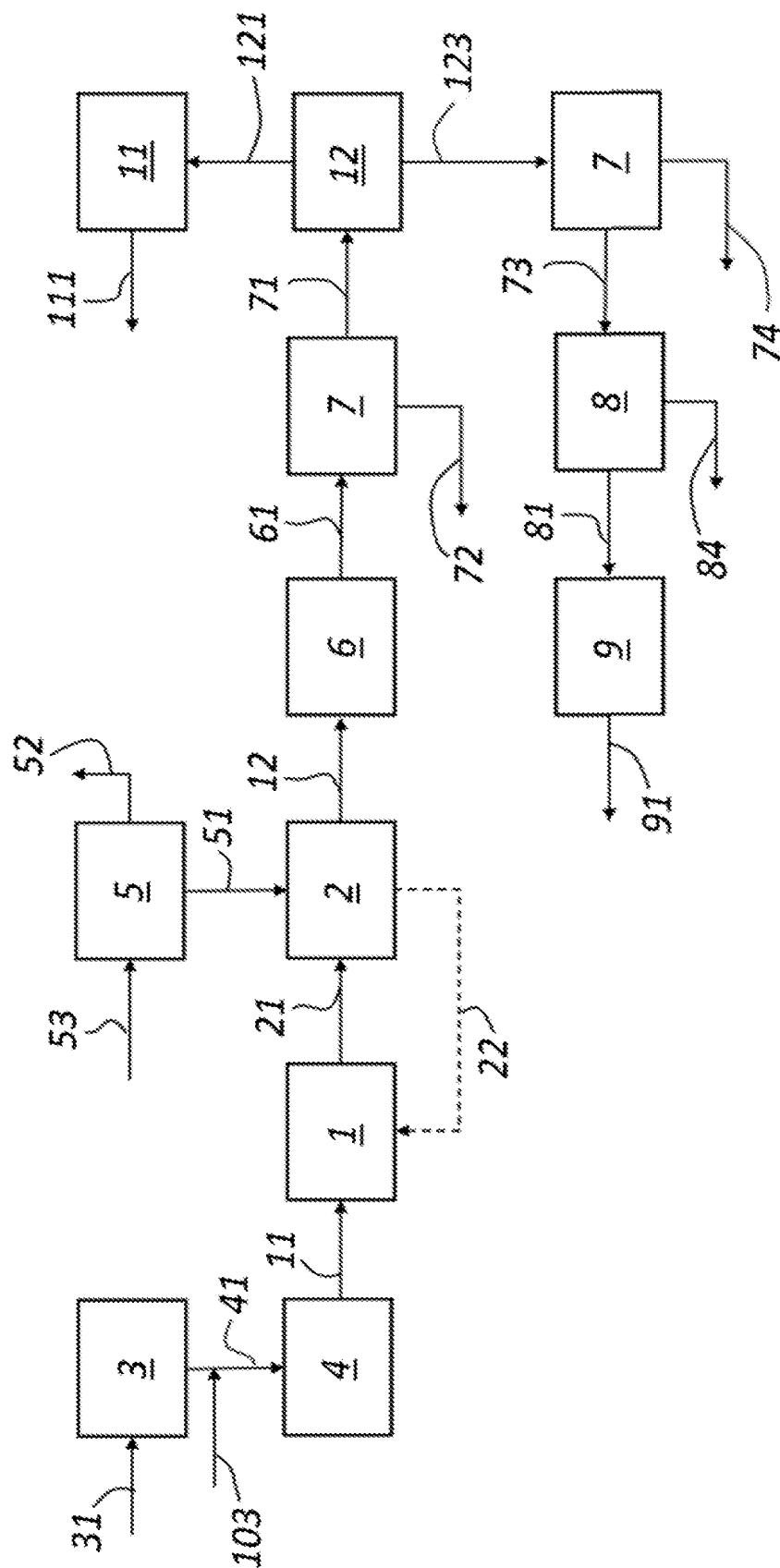
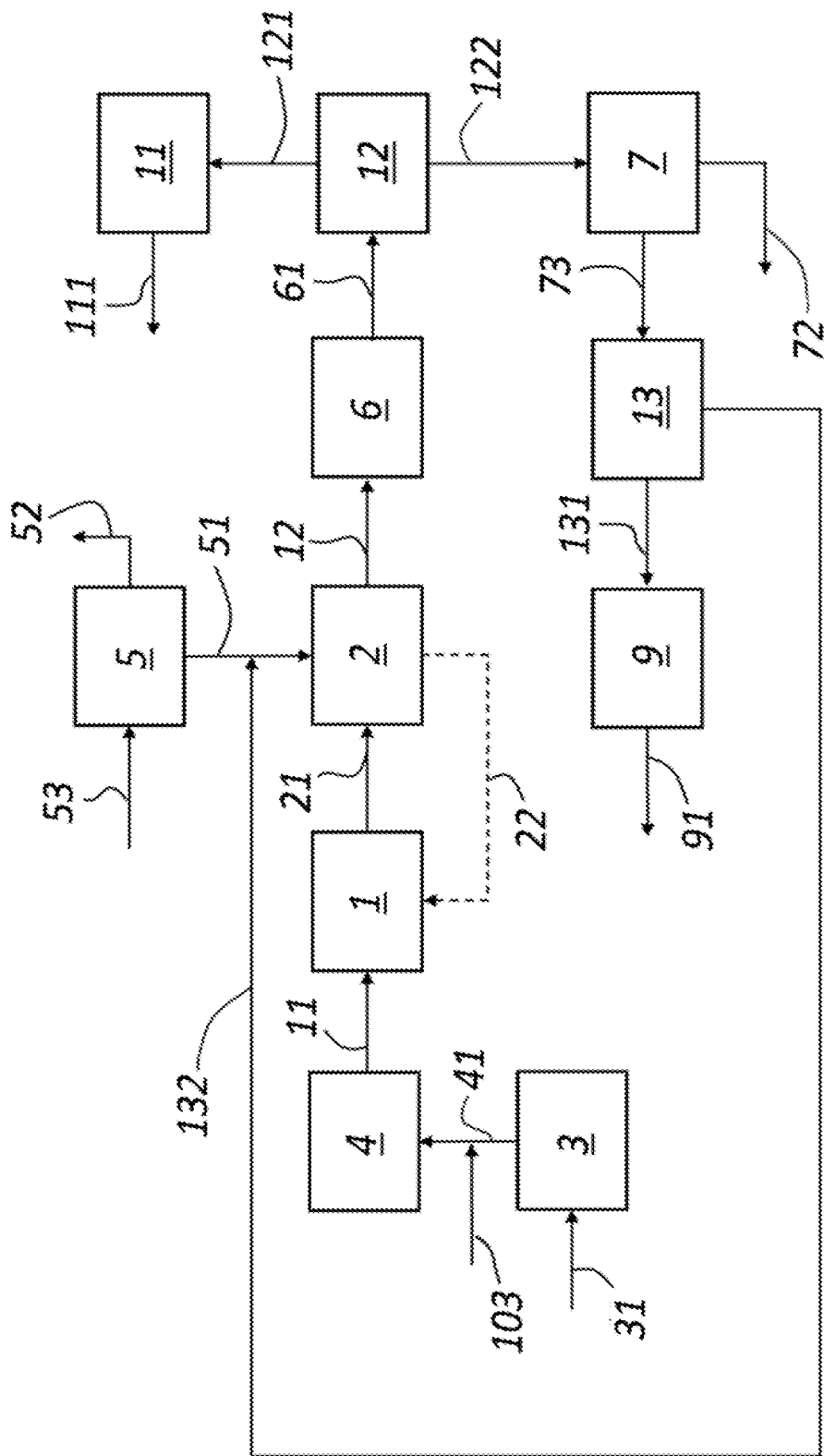


FIGURE 5





## FIGURE 7

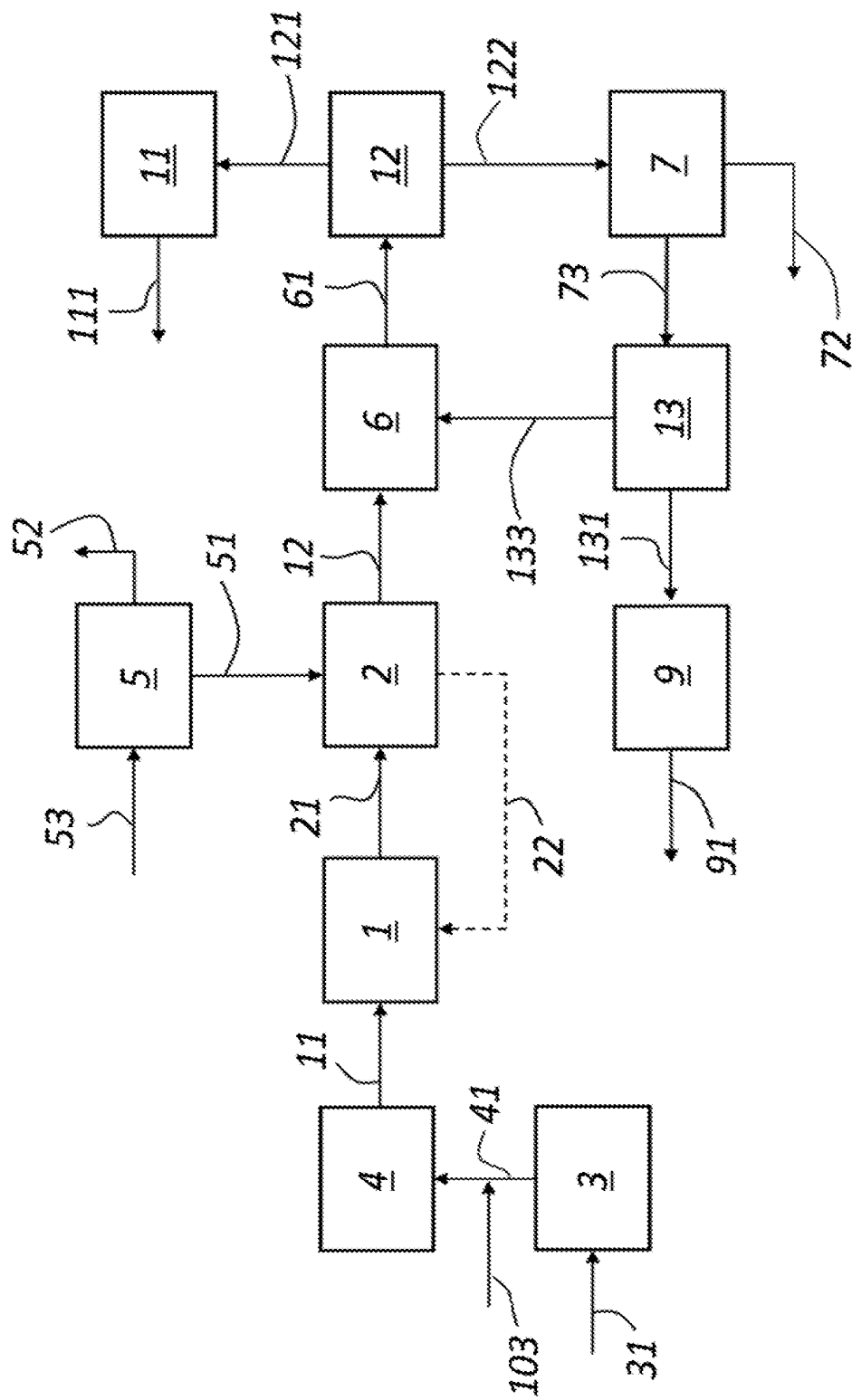


FIGURE 8

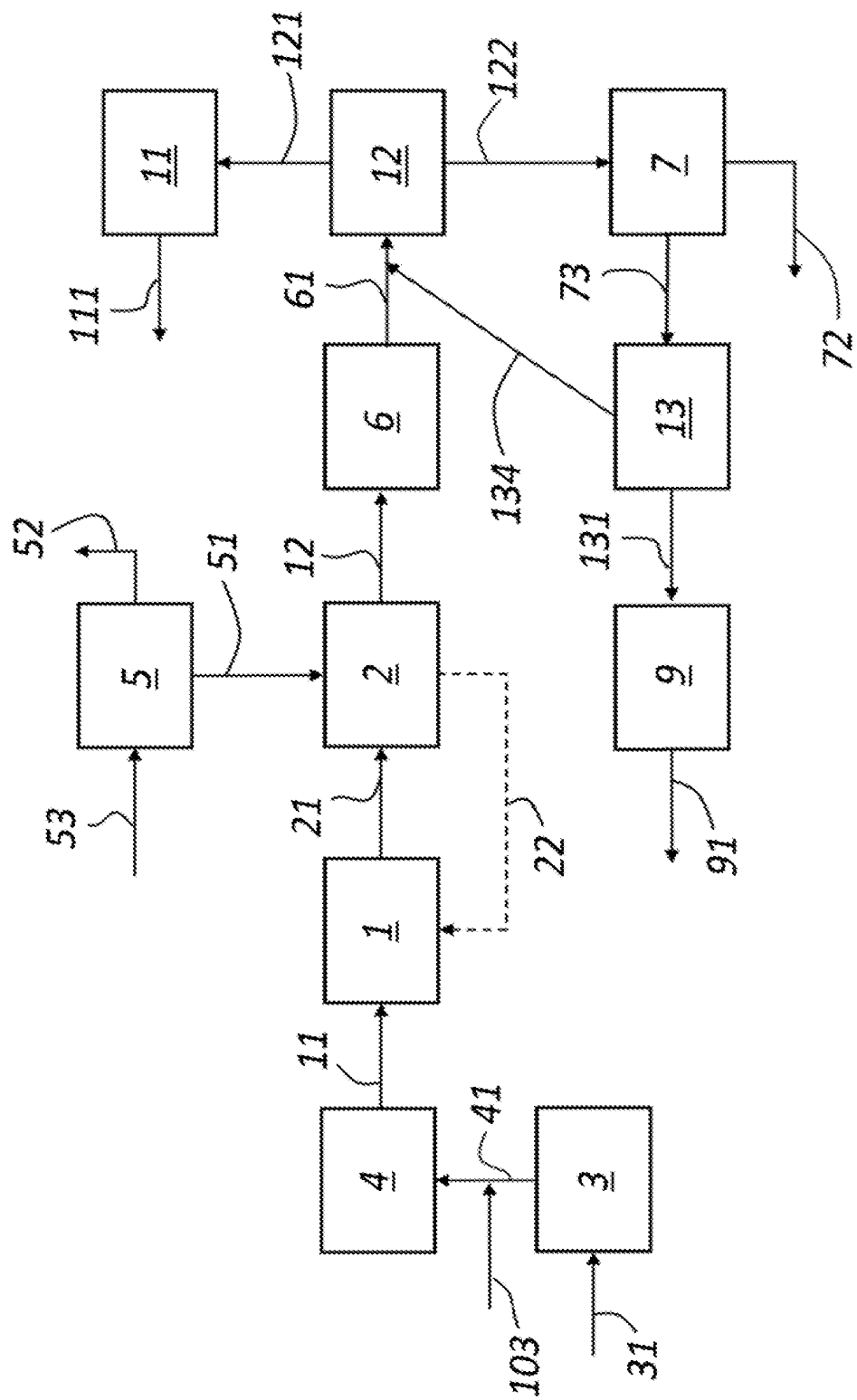


FIGURE 9

Table 1. Summary of process schemes.

|                                          | Comparative<br>Example | Embodiment<br>Example 1 | Embodiment<br>Example 2 | Embodiment<br>Example 3 | Embodiment<br>Example 4 | Embodiment<br>Examples 5-<br>7 |
|------------------------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------|
| WGS temperature<br>(°C)                  | 256                    | 300                     | 300                     | 256                     | 256                     | 300                            |
| Pd membrane                              |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Water condensation<br>directly after WGS | ✓                      |                         |                         | ✓                       | ✓                       |                                |
| Water condensation<br>after membrane     |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Amine separation                         | ✓                      | ✓                       |                         | ✓                       |                         |                                |
| Cryogenic<br>separation                  |                        |                         | ✓                       |                         | ✓                       | ✓                              |
| PSA                                      | ✓                      |                         |                         |                         |                         |                                |
| Recycle of rest-gas                      |                        |                         |                         |                         |                         | ✓                              |

FIGURE 10



Table 2.

| Type                                   | Comparative Example | Embodiment Example 1 | Embodiment Example 2  | Embodiment Example 3  | Embodiment Example 4  |
|----------------------------------------|---------------------|----------------------|-----------------------|-----------------------|-----------------------|
|                                        |                     | Membrane after WGS   | Membrane after heater | Membrane after heater | Membrane after heater |
|                                        | Base case           | Pd + Amine           | Pd + Cryo             | Pd + Amine            | Pd + Cryo             |
| H <sub>2</sub> production (kg/h)       | 1412                | 1516                 | 1516                  | 1524                  | 1524                  |
| H <sub>2</sub> production (kmol/h)     | 701                 | 752                  | 752                   | 756                   | 756                   |
| H <sub>2</sub> recovery factor (%)     | 86                  | 93                   | 93                    | 93                    | 93                    |
| Carbon capture (%) <sup>*</sup>        | 97.5                | 96                   | 90                    | 96                    | 90                    |
| CO <sub>2</sub> before capture (mol%)  | 25                  | 79                   | 79                    | 80                    | 80                    |
| Purity of CO <sub>2</sub> captured (%) | 100                 | 100                  | 99.9                  | 100                   | 99.9                  |
| CO conversion in WGS                   | 97.4                | 95.0                 | 95.0                  | 97.4                  | 97.4                  |

<sup>\*</sup> Defined as carbon captured relative to carbon in feed

FIGURE 11

Table 3. Advantages of the different examples.

| Type                                    | Comparative Example | Embodiment Example 1 | Embodiment Example 2  | Embodiment Example 3  | Embodiment Example 4  |
|-----------------------------------------|---------------------|----------------------|-----------------------|-----------------------|-----------------------|
|                                         |                     | Membrane after WGS   | Membrane after heater | Membrane after heater | Membrane after heater |
|                                         | Base case           | Pd + Amine           | Pd + Cryo             | Pd + Amine            | Pd + Cryo             |
| Cost of H <sub>2</sub> separation       |                     | +++                  | +++                   | +++                   | +++                   |
| Footprint of H <sub>2</sub> separation  |                     | ++                   | ++                    | ++                    | ++                    |
| Efficiency of H <sub>2</sub> separation |                     | +++                  | +++                   | +++                   | +++                   |
| Cost of CO <sub>2</sub> separation      |                     | +                    | ++                    | +                     | ++                    |
| Footprint of CO <sub>2</sub> separation |                     | +                    | ++                    | +                     | ++                    |
| Efficiency of CO <sub>2</sub> capture   | ++                  | +                    |                       | +                     |                       |
| Water condensation                      | ++                  | ++                   | ++                    |                       |                       |
| Heat exchange                           | ++                  | +                    | +                     |                       |                       |
| Total                                   | 6+                  | 14+                  | 15+                   | 11+                   | 12+                   |

FIGURE 12

Table 4. Effect of recycling rest-gas to ATR.

|                                     | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Recycle option                      | No recycle              | 50%                     | 80%                     | 90%                     |
| O <sub>2</sub> to ATR (kg/h)        | 4179                    | 4316                    | 4426                    | 4482                    |
| H <sub>2</sub> production (kmol/h)  | 752                     | 777                     | 794                     | 799*                    |
| Carbon capture (%)                  | 89.7                    | 94.4                    | 97.7                    | 98.8                    |
| Heat available in Fired heater (MW) | 4.6                     | 2.5                     | 1.0                     | 0.5                     |

\* Represents 99% hydrogen recovery compared to Table 2.

FIGURE 13

Table 5. Advantages of Embodiment Examples 5-7.

|                                         | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|                                         | No recycle              | 50 %                    | 80 %                    | 90 %                    |
| Cost of H <sub>2</sub> separation       | +++                     | +++                     | +++                     | +++                     |
| Footprint of H <sub>2</sub> separation  | ++                      | ++                      | ++                      | ++                      |
| Efficiency of H <sub>2</sub> separation | +++                     | +++                     | ++++                    | ++++                    |
| Cost of CO <sub>2</sub> separation      | ++                      | ++                      | ++                      | ++                      |
| Footprint of CO <sub>2</sub> separation | ++                      | ++                      | ++                      | ++                      |
| Efficiency of CO <sub>2</sub> capture   |                         | +                       | ++                      | +++                     |
| Water condensation                      | ++                      | ++                      | ++                      | ++                      |
| Heat exchange                           | +                       | +                       | +                       | +                       |
| Energy efficiency                       | ++                      | +                       |                         |                         |
| Total                                   | 17+                     | 17+                     | 18+                     | 19+                     |

FIGURE 14

Table 6. Effect of recycling 80% rest-gas compared to no recycle.

|                                        | Embodiment<br>Example 2 | Embodiment<br>Example 6 | Embodiment<br>Example 8 | Embodiment<br>Example 9 | Embodiment<br>Example 10 |
|----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| Recycle option                         | No recycle              | To ATR                  | To WGS                  | To<br>membrane          | To ATR                   |
| Recycle ratio                          | 0%                      | 80%                     | 80%                     | 80%                     | 80%                      |
| O <sub>2</sub> to ATR (kg/h)           | 4179                    | 4426                    | 4179                    | 4179                    | 4179                     |
| ATR exit (°C)                          | 1020                    | 1020                    | 1020                    | 1020                    | 989                      |
| H <sub>2</sub> production (kmol/h)     | 752                     | 798                     | 803                     | 797                     | 807                      |
| Carbon capture (%)                     | 89.7                    | 97.7                    | 97,3                    | 95,1                    | 97,5                     |
| Heat available in Fired<br>heater (MW) | 4.6                     | 1.0                     | 1,5                     | 1,9                     | 1.2                      |

FIGURE 15

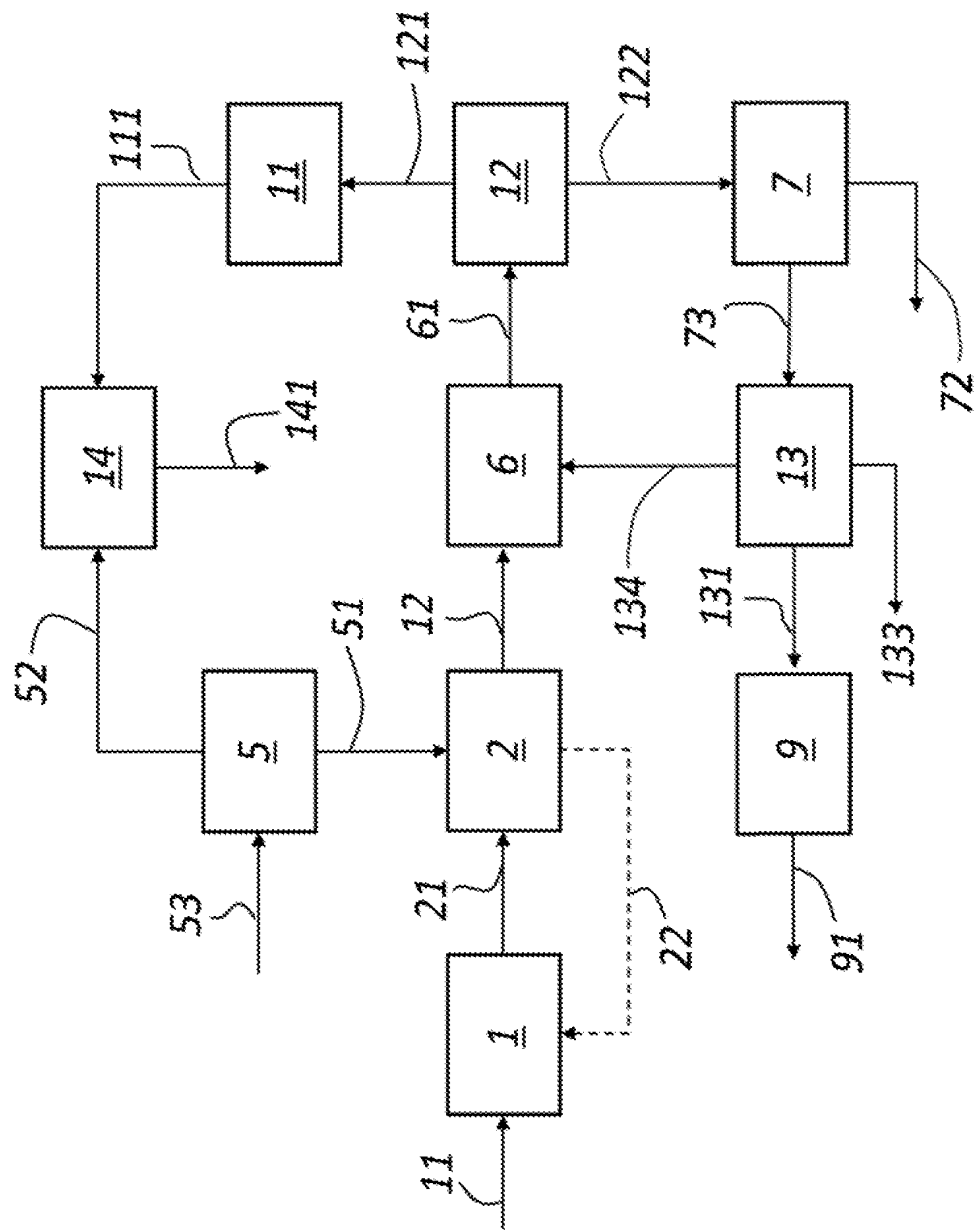


FIGURE 16

## **DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)**

|                                              |                                                |
|----------------------------------------------|------------------------------------------------|
| International application number:            | <b>PCT/EP2021/054441</b>                       |
| International filing date:                   | <b>23 February 2021 (23.02.2021)</b>           |
| Document type:                               | <b>Certified copy of priority document</b>     |
| Document details:                            | Country/Office: <b>GB</b>                      |
|                                              | Number: <b>2003317.1</b>                       |
|                                              | Filing date: <b>06 March 2020 (06.03.2020)</b> |
| Date of receipt at the International Bureau: | <b>06 March 2021 (06.03.2021)</b>              |

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-bis)

Form PTO-1449 (Modified)

**INFORMATION DISCLOSURE STATEMENT**Atty. Docket No.  
2110-0010Serial No.  
Not Yet  
AssignedInventor(s)  
Torkild R. Reinertsen et al.Filing Date  
February 23, 2021Art Unit  
Not Yet  
Assigned**U.S. PATENT DOCUMENTS**

| Examiner Initials | Document Number | Issue or Publication Date | Name               | Class | Subclass | Filing Date (If Appropriate) |
|-------------------|-----------------|---------------------------|--------------------|-------|----------|------------------------------|
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|                   | 2014/0170052    | 06-19-2014                | Iaquaniello et al. |       |          |                              |
|                   | 2014/0186255    | 07-03-2014                | Jadhav             |       |          |                              |

**FOREIGN PATENT DOCUMENTS**

| Examiner Initials | Document Number | Publication Date | Country                       | Translation |    |
|-------------------|-----------------|------------------|-------------------------------|-------------|----|
|                   |                 |                  |                               | Yes         | No |
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|                   | GB 2571136      | 08-21-2019       | Great Britain                 | N/A         |    |
|                   | WO91/12200      | 08-22-1991       | World Intellectual Prop. Org. | See IDS     |    |
|                   | WO2009/088971   | 07-16-2009       | World Intellectual Prop. Org. | N/A         |    |
|                   | WO2019/162236   | 08-29-2019       | World Intellectual Prop. Org. | N/A         |    |
|                   | WO2020/012018   | 01-16-2020       | World Intellectual Prop. Org. | N/A         |    |

EXAMINER:

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|                          |                                             |                                   |
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| Form PTO-1449 (Modified) | Atty. Docket No.<br>2110-0010               | Serial No.<br>Not Yet<br>Assigned |
|                          | Inventor(s)<br>Torkild R. Reinertsen et al. |                                   |
|                          | Filing Date<br>February 23, 2021            | Art Unit<br>Not Yet<br>Assigned   |

**INFORMATION DISCLOSURE STATEMENT****OTHER DOCUMENTS**

|  |                                                                                                                                  |
|--|----------------------------------------------------------------------------------------------------------------------------------|
|  | Combined Search and Examination Report, counterpart App. No. GB2003317.1 (April 2, 2020) (5 pages)                               |
|  | Combined Search and Examination Report, counterpart App. No. GB2010174.7 (August 4, 2020) (8 pages)                              |
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|  | ROSTRUP-NIELSEN, <i>Production of synthesis gas</i> , Catalysis Today, Vol. 18, pp. 305-324 (1993).                              |
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|  |                                                                                                                                  |

EXAMINER:

DATE CONSIDERED:

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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     | Not yet assigned                           |
| Filing Date            | February 23, 2021                          |
| First Named Inventor   | Torkild R. Reinertsen                      |
| Title                  | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |
| Art Unit               | Not yet assigned                           |
| Examiner Name          | Not yet assigned                           |
| Attorney Docket Number | 2110-0010                                  |

### SIGNATURE of Applicant or Patent Practitioner

|                                                    |                  |                     |                   |
|----------------------------------------------------|------------------|---------------------|-------------------|
| Signature                                          | /Paul C. Craane/ | Date (Optional)     | September 1, 2022 |
| Name                                               | Paul C. Craane   | Registration Number | 38,851            |
| Title (if Applicant is a juristic entity)          |                  |                     |                   |
| Applicant Name (if Applicant is a juristic entity) |                  |                     |                   |

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



\*Total of 1 forms are submitted.

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Inventor or Joint Inventor (title not required below)



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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)

23. August 2022

Name

Geir Suul

Title

CEO

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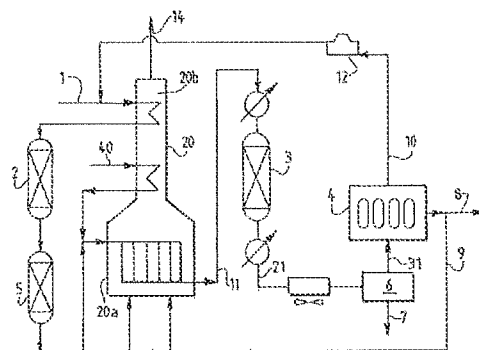
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⑸ PROCÉDE DE FABRICATION D'UN GAZ DE SYNTHÈSE OU D'HYDROGÈNE, A PARTIR D'UNE CHARGE  
HYDROCARBONÉE.

⑹ L'invention concerne un procédé de fabrication d'un  
gaz de synthèse ou d'hydrogène, à partir d'une charge hy-  
drocarbonée (1), dans lequel on transforme la charge hy-  
drocarbonée principalement en hydrogène dans un four  
(20) de type vaporéformage du méthane, dans lequel on  
traite le flux gazeux (11) ainsi produit pour en éliminer le  
dioxyde de carbone et en purifier la teneur en hydrogène,  
dans lequel une partie de l'hydrogène obtenu en sortie des  
étapes ci-avant mentionnées, est utilisée en amont du pro-  
cédé pour alimenter la combustion dudit four. Avantageuse-  
ment, au moins un flux gazeux, issu des moyens de  
purification dudit flux gazeux produit à la sortie du four, est  
recyclé en amont du procédé comme charge hydrocarbo-  
née additionnelle.



FR 2 949 772 - A1



**PROCEDE DE FABRICATION D'UN GAZ DE SYNTHESE OU  
D'HYDROGENE, A PARTIR D'UNE CHARGE HYDROCARBONEE**

L'invention concerne un procédé de fabrication d'un gaz de synthèse ou d'hydrogène, à partir d'une charge hydrocarbonée ou analogue, dans lequel on transforme la charge hydrocarbonée principalement en gaz de synthèse ou hydrogène dans un four de type vaporéformage ou de type réformage autotherme ou analogue, dans lequel on traite le flux gazeux ainsi produit pour en éliminer le dioxyde de carbone et en purifier la teneur en hydrogène, dans lequel une partie de l'hydrogène obtenu en sortie des étapes ci-avant mentionnées, est utilisée en amont du procédé pour alimenter la combustion dudit four. De façon optionnelle et avantageuse, un flux gazeux riche en hydrocarbure ou en monoxyde de carbone issu des moyens de séparation et purification dudit flux gazeux produit dans le procédé en aval de la sortie du four, est recyclé en amont du procédé comme charge hydrocarbonée additionnelle.

L'invention se situe plus particulièrement dans le domaine de la fabrication de gaz de synthèse ou d'hydrogène à partir d'une charge hydrocarbonée, en utilisant par exemple un four de type vaporéformage (connu pour une charge hydrocarbure méthane sous le sigle SMR qui provient de l'anglais « steam methane reforming » qui signifie « réformage du méthane à la vapeur ») ou réformage dit autotherme (connu sous le sigle ATR qui provient de l'anglais « autothermal reformer » qui signifie réformeur autotherme, ou auto-thermique), dont la chaleur de combustion est généralement produite par le brûlage d'un combustible de type hydrocarbure.

Le but principal de l'invention est de réduire le plus possible la teneur en dioxyde de carbone (CO<sub>2</sub>) dans les fumées du four en utilisant comme combustible de l'hydrogène produit dans le procédé. En effet, ces fumées qui ont une pression partielle en CO<sub>2</sub> faible et qui contiennent aussi d'autres gaz tels que de l'oxygène, de la vapeur d'eau, et de l'azote, ne sont pas faciles à traiter. A ce sujet, on peut se référer à la publication intitulée « Post-combustion capture of CO<sub>2</sub> » de Sulzer Chemtech parue dans la revue PTQ (Q2-2009).

Un autre but de l'invention est de fournir un dispositif de séparation du dioxyde de carbone issu du procédé de fabrication du gaz de synthèse en vue d'une séquestration séparée ultérieure.

Comme déjà évoqué plus haut, pour l'ingénieur du métier qui  
5 cherche à éliminer le CO<sub>2</sub> produit dans un procédé, par exemple de fabrication d'un gaz de synthèse, la solution la plus évidente est d'essayer de capter le CO<sub>2</sub> présent dans la partie du procédé qui fonctionne à plus haute pression, c'est-à-dire à l'endroit où circule le flux gazeux principal produit dans le procédé. Or, ce flux gazeux ne  
10 représente qu'une partie (typiquement de l'ordre de 55% poids dans une unité SMR avec charge méthane), même si elle est non négligeable, du CO<sub>2</sub> généré dans le procédé. Le reste du CO<sub>2</sub> (environ 45% poids) est émis par les fumées du four pour lesquelles les procédés de traitement existants sont difficiles à mettre en œuvre compte tenu de  
15 la faible pression des fumées et des volumes importants de gaz à traiter. Cela oblige en particulier à augmenter notablement la pression de gros volumes de gaz, et en conséquence, l'homme du métier n'envisage que rarement de capter le CO<sub>2</sub> généré au niveau des fumées du four car le coût de l'opération s'avère excessivement élevé.

L'invention proposée par la Demanderesse permet une capture  
20 quasi totale du CO<sub>2</sub> productible dans le procédé. Elle est principalement caractérisée par le fait que, de manière surprenante, on prélève une partie de l'hydrogène produit dans le procédé afin de l'utiliser comme combustible du four de production d'hydrogène ou de  
25 gaz de synthèse.

Cette disposition peut paraître surprenante car l'hydrogène est coûteux, mais la Demanderesse a démontré sur des exemples que la production nette d'hydrogène ou de gaz de synthèse est peu affectée  
30 par cet usage d'hydrogène dans le four, car le combustible de type fuel-gaz qui est ainsi économisé au lieu d'être brûlé dans le four, peut être utilisé comme charge additionnelle du procédé et par conséquent être transformé en hydrogène. Ce fuel-gaz économisé devient ainsi lui-même source additionnelle d'hydrogène.

Des procédés de production de gaz de synthèse et d'hydrogène  
35 sont déjà connus. Par exemple, le brevet US7.405.243 de CHEVRON décrit un procédé de synthèse d'hydrocarbures, par exemple du type Fischer-Tropsch, permettant d'obtenir avec d'autres coupes

d'hydrocarbures, après traitement, un hydrogène de grande pureté. Cette invention envisage plusieurs utilisations possibles pour cet hydrogène, par exemple dans divers procédés d'hydrotraitement de produits hydrocarbures ou de régénération de catalyseurs.

5 L'invention décrite par le brevet FR 2.890.655 de l'Air Liquide, concerne un procédé de conversion de gaz hydrocarbonés en liquides hydrocarbonés dans lequel on met en œuvre :

- dans une première étape, la conversion des gaz hydrocarbonés en gaz de synthèse,
- 10 - dans une deuxième étape, le procédé Fischer-Tropsch produisant un gaz résiduaire contenant de l'hydrogène,
- dans une troisième étape, un hydrocraquage au moyen d'un gaz hydrogéné, dans lequel le gaz hydrogéné est produit par un procédé de purification PSA du gaz résiduaire issu du procédé Fischer-Tropsch et d'un effluent gazeux riche en hydrogène issu d'une unité de
- 15 réformage de méthane à la vapeur.

Cependant, bien que relevant du domaine de la présente invention, aucune des deux références précitées ne décrit ni ne suggère les caractéristiques de l'invention, et en particulier l'utilisation de

20 l'hydrogène pour alimenter une combustion de four de SMR ou analogue.

La présente invention, consistant à utiliser de l'hydrogène pur comme combustible du four et, dans une variante avantageuse, à recycler certains flux de purge de séparation comme charge

25 hydrocarbonée additionnelle en amont du procédé, permet ainsi d'éliminer la présence de CO<sub>2</sub> dans les fumées du four et de ce fait limiter le problème de la captation du CO<sub>2</sub> à un nombre restreint de flux de procédé, qui fonctionnent en pression relativement élevée. Un module de séparation approprié installé sur le flux principal du gaz de

30 synthèse permettra d'extraire le CO<sub>2</sub> en vue d'une captation séparée du CO<sub>2</sub> qui pourra ensuite être récupéré d'une manière appropriée.

Les options technologiques ainsi retenues pourront générer quelques inconvénients tels que le léger surdimensionnement de l'unité SMR et le surinvestissement en principe modéré correspondant, mais

35 cela vaut le prix à payer pour la capture quasi-complète du CO<sub>2</sub> dans le procédé. La maîtrise de la combustion d'hydrogène nécessite aussi certaines précautions, le pouvoir calorifique volumique de l'hydrogène



étant plus faible que celui des hydrocarbures habituellement utilisés. En phase de démarrage du four, sauf à avoir stocké de l'hydrogène, il faudra brûler un autre combustible et émettre du CO<sub>2</sub>. Durant cette phase transitoire, ce combustible annexe sera utilisé jusqu'au moment où la production d'hydrogène sera bien établie, et autorisera ainsi de basculer l'alimentation des brûleurs du four sur l'hydrogène. Ce même combustible annexe pourra être utilisé dans certaines phases transitoires pendant lesquelles la production d'hydrogène deviendrait momentanément insuffisante, comme par exemple pendant un déclenchement inopiné d'une unité aval de séparation purification du flux hydrogène.

Ainsi la présente invention décrit un procédé de fabrication d'un gaz de synthèse ou d'hydrogène, à partir d'une charge hydrocarbonée ou analogue, dans lequel on transforme la charge hydrocarbonée en gaz de synthèse contenant de l'hydrogène dans un four de type vaporéformage ou de type réformage autotherme ou analogue, dans lequel on traite le gaz de synthèse par des moyens de traitement pour la séparation et/ou purification de l'hydrogène contenu dans le gaz de synthèse, caractérisé en ce qu'une partie au moins de l'hydrogène ainsi produit est prélevée et renvoyée en amont du procédé pour alimenter la combustion dudit four.

De façon optionnelle et avantageuse, au moins une partie du flux gazeux hydrocarboné issu des moyens de traitement et/ou de la transformation de la charge en gaz de synthèse, ce flux étant notamment un flux gazeux riche en hydrocarbure ou en monoxyde de carbone, est prélevée et recyclée en amont du procédé comme charge hydrocarbonée additionnelle du procédé.

Les moyens de traitement du gaz de synthèse formant le flux gazeux principal comprennent un réacteur de conversion du CO à la vapeur (ou « water gas shift » en anglais, expression la plus souvent utilisée), une unité de séparation du dioxyde de carbone et une unité de séparation et de purification d'hydrogène.

Un « water gas shift » est une unité connue de l'homme de l'art, qui permet de réduire la teneur en CO du gaz traité et d'augmenter sa teneur en hydrogène (en réalisant la réaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ) jusqu'à obtenir un rapport H<sub>2</sub>/CO dans le gaz traité—qui est adapté à une transformation ultérieure de ce gaz de synthèse en hydrocarbures

liquides par synthèse chimique selon divers procédés connus (par exemple le procédé « Fischer-Tropsch » pour lequel un rapport  $H_2/CO$  voisin de 2 est nécessaire).

5 L'unité de séparation du dioxyde de carbone permet la séparation du  $CO_2$  en vue d'une captation ultérieure.

Avantageusement, le dioxyde de carbone formé peut être partiellement utilisé comme agent oxydant du procédé dans le four de réformage, c'est-à-dire qu'une partie de ce dioxyde de carbone formé est renvoyée en tant qu'oxydant, ou en d'autres termes que le  $CO_2$  est renvoyé au four comme agent oxydant en complément d'un autre agent oxydant, qui est soit de la vapeur d'eau pour le SMR ou de l'oxygène pour le four autotherme.

15 Cette unité de séparation du dioxyde de carbone peut être du type mettant en œuvre des solvants chimiques, type amines ou équivalents.

Selon un mode de réalisation préféré de l'invention, l'unité de séparation du dioxyde de carbone est du type mettant en œuvre le procédé dit « Benfield », bien connu de l'homme du métier.

20 L'unité de séparation du dioxyde de carbone peut également être du type mettant en œuvre des solvants physiques, de type « Rectisol® » ou analogue.

L'unité de séparation du dioxyde de carbone peut encore être du type mettant en œuvre des séparations par moyens physiques du type tamis moléculaires ou du type membrane.

25 D'autres procédés peuvent être mis en œuvre comme par exemple le procédé « Econamine FG » commercialisé par la société américaine d'ingénierie Fluor Daniel, ou des unités à fonctionnement cryogénique. L'unité de séparation du dioxyde de carbone installée sur le flux procédé principal peut être située en amont ou en aval de l'unité PSA précédemment citée selon les procédés mis en œuvre et suivant des considérations d'optimisation techniques et économiques retenues.

30 Selon une particularité avantageuse de l'invention, tout ou partie d'un gaz de purge issu de l'unité de séparation et de purification d'hydrogène est recyclée en amont du procédé comme charge hydrocarbonée additionnelle.

35 Selon un mode préféré de réalisation de l'invention, dans le cas d'une unité visant à produire essentiellement de l'hydrogène (telle que

le décrira plus loin dans la description la figure 1), l'unité de séparation et de purification d'hydrogène est de type PSA (« Pressure swing adsorption »).

5 Le gaz de purge issu d'une telle unité PSA contient alors du monoxyde de carbone, du dioxyde de carbone, ainsi que de l'hydrogène et du méthane résiduels. En recyclant ainsi dans la charge des molécules de type  $\text{CH}_4$  notamment qui ne sont pas directement valorisables en l'état en aval du procédé, on compense partiellement la

10

Selon un autre mode préféré de réalisation de l'invention, dans le cas d'une unité visant à produire essentiellement un gaz de synthèse pour alimenter une unité Fischer Tropsch telle que décrite ci-après en détails à la figure 2, ou pour une unité de synthèse de méthanol ou

15 d'autres applications analogues, l'unité de séparation et de purification d'hydrogène est de type à membrane permettant de prélever la quantité d'hydrogène (en flux basse pression en sortie membrane) nécessaire pour alimenter le four.

20 L'unité de séparation et de purification de l'hydrogène est par exemple du type à membrane du genre « Medal® ».

Les boucles de régulation de pression, permettant d'assurer le prélèvement de la quantité d'hydrogène nécessaire et l'obtention du bon ratio  $\text{H}_2/\text{CO}$  dans le flux principal, seront mises en place à cet effet sans difficulté particulière selon les règles de l'homme de l'art.

25 Dans le cas d'une unité de production de gaz de synthèse, le flux recyclé dans la charge de l'unité de réformage sera constitué préférentiellement par les molécules résiduelles de monoxyde et dioxyde de carbone, d'hydrogène et de méthane sortant de l'étape de synthèse après séparation des produits recherchés (hydrocarbure  $\text{C}_5+$ , ou méthanol, ou alcools lourds).

30

Cependant, l'unité de séparation et de purification de l'hydrogène peut également être du type PSA.

Par ailleurs, l'utilisation d'hydrogène comme combustible du four procure une opportunité d'améliorer le rendement utile du four.

35 Ainsi, selon un autre mode de réalisation préféré de l'invention, on peut récupérer la chaleur des fumées à base de vapeur d'eau produites par la combustion de l'hydrogène dans le four, par exemple

par condensation de la vapeur d'eau présente dans les fumées du four, pour le préchauffage d'eau de chaudière du procédé et/ou préférentiellement pour le préchauffage de la charge hydrocarbonée d'alimentation du four. On augmente ainsi le rendement de  
5 fonctionnement du four et plus marginalement (de quelques pourcents) le rendement de fabrication du gaz produit final.

Notamment, la chaleur peut être récupérée jusqu'à condensation partielle ou totale de la vapeur d'eau contenue dans les fumées.

La charge hydrocarbonée du procédé selon l'invention peut être  
10 du méthane et le four être un four à vaporéformage, le méthane subissant un réformage à la vapeur.

En variante, la charge hydrocarbonée du procédé selon l'invention peut être du méthane ou du naphtha, et le four peut être un four autotherme, la charge hydrocarbonée subissant un réformage  
15 autotherme.

Dans le cas d'une mise en œuvre en amont d'une turbine à gaz ou « TAG », un SMR fonctionnant au gaz naturel produisant de l'hydrogène selon l'invention proposée, permettrait d'alimenter la TAG avec de l'hydrogène pour combustion, le rejet de CO<sub>2</sub> étant canalisé en  
20 regard du SMR, en amont de la TAG. C'est vraisemblablement une des rares solutions imaginables pour disposer d'une TAG intégrant une capture complète du CO<sub>2</sub> associé et applicables à d'autres combustibles fossiles gazeux ou rendus gazeux.

On peut aussi avantageusement citer l'exemple d'une raffinerie  
25 qui s'attaquerait à la capture du CO<sub>2</sub> en vue d'une séquestration ultérieure, et qui suivant la solution inventive décrite pourrait à cet effet installer un SMR dédié pour transformer, de façon centralisée et en vue de maximiser les quantités captées, les combustibles des fours (fuel-gaz produit par les unités de la raffinerie, gaz naturel additionnel,  
30 voire un combustible hydrocarbure liquide, par exemple une coupe essence ou gazole), en hydrogène au lieu de les envoyer directement pour combustion dans les fours et/ou chaudières de la raffinerie. Le principal bénéfice est de réaliser de la sorte une séparation de CO<sub>2</sub> en un point unique déterminé au lieu de multiplier les points de  
35 séparation correspondant à plusieurs dizaines de fours ou de chaudières pour une raffinerie classique, permettant de résoudre la difficulté antérieurement décrite de réaliser un captage sur les fumées.

Le réformage à la vapeur étant lui même producteur net de vapeur dans certaines configurations de procédé, une telle solution pourra avantageusement remplacer partiellement une capacité de chaudière à construire, ce qui peut contribuer à justifier plus aisément la mise en œuvre économique du schéma ainsi retenu. Suivant le même principe, toute industrie utilisatrice de gaz (autoproduits ou gaz naturels importés dans son enceinte) dans des fours ou chaudières, à l'exemple de la sidérurgie, pourra décliner le même type de solution.

Dans les exemples précédents, il sera opportun comme décrit antérieurement, de profiter si possible de la condensation des vapeurs d'eau dans les fumées du four pour accroître les rendements thermiques des unités utilisatrices de chaleur.

Avantageusement, les produits non recherchés, après l'étape finale de transformation du gaz de synthèse en produits commercialisables, seront séparés et recyclés dans le procédé de réformage amont.

L'invention est maintenant décrite en référence aux dessins annexés, non limitatifs, dans lesquels :

- la figure 1 est un schéma synoptique d'un procédé selon l'invention, illustrant l'application à la production d'hydrogène par vaporéformage du méthane ;
- la figure 2 est un schéma synoptique d'une variante de procédé selon l'invention, illustrant l'application à la production d'hydrogène par réformage autotherme et synthèse de type Fischer-Tropsch.

Dans l'installation de la figure 1, la charge hydrocarbonée 1 (du méthane ou gaz naturel en l'occurrence) est préchauffée par échange thermique dans la partie haute 20b du vaporéformeur de méthane 20, appelée généralement section de convection. Ce type de vaporéformeur est bien connu de l'homme du métier. Par exemple, le brevet FR 2.904.830 de l'IFP, cité ici à titre de référence, en donne une description détaillée. Un fabricant bien connu également de ce type d'équipement est Foster Wheeler qui le commercialise notamment sous la marque déposée « Terrace-Wall™ ».

La charge hydrocarbonée 1, après ajout d'hydrogène et préchauffage dans divers échangeurs de chaleur, est ensuite prétraitée dans un réacteur d'hydrogénation 2, puis dans un réacteur de

désulfuration 5, avant d'être envoyée dans la partie catalytique 20a du vaporéformeur 20 où elle réagit en présence de vapeur d'eau pour obtenir un gaz de synthèse 11 qui contient principalement, hors vapeur d'eau, un mélange d'oxydes de carbone et d'hydrogène.

5           Le gaz de synthèse 11 est ensuite envoyé dans un réacteur de conversion 3 du CO à la vapeur d'eau (ou « water gas shift » en anglais, expression la plus souvent utilisée) qui permet de réduire la teneur en CO du gaz traité et d'augmenter sa teneur en hydrogène (en réalisant la réaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ). La vapeur d'eau nécessaire est  
10       produite essentiellement dans la convection du four à partir d'une eau déminéralisée 40 et est introduite généralement dans le flux procédé en amont du four.

          Le gaz de synthèse 21 ainsi traité est ensuite envoyé dans une unité de séparation du dioxyde de carbone 6 au moyen de laquelle le  
15       CO<sub>2</sub> séparé 7 pourra ensuite être dirigé vers des moyens de captation ou de stockage appropriés. Ces moyens, qui ne font pas partie de l'invention à proprement parler, sont connus de l'homme du métier et font l'objet actuellement de développements et d'expérimentations nombreux et variés. On citera à titre d'exemple la séquestration  
20       géologique dans d'anciens réservoirs de gaz ou de pétrole.

          L'unité de séparation 6 du dioxyde de carbone est par exemple du type bien connu mettant en œuvre le procédé dit « Benfield », couramment licenciée par la société américaine UOP (Groupe Honeywell). D'autres procédés de même finalité sont décrits dans la  
25       littérature et on pourra se référer en particulier à la publication intitulée « Recovery of CO<sub>2</sub> from Flue Gases : Commercial Trends », initialement présentée à la réunion annuelle de la « Canadian Society of Chemical Engineers », 4-6 Octobre 1999, Saskatoon, Saskatchewan, Canada, par Dan G. Chapel et Carl L. Mariz de la société américaine  
30       Fluor Daniel.

          Le gaz de synthèse 31 quittant l'unité de séparation de CO<sub>2</sub>, 6, traverse ensuite une unité de séparation et de purification d'hydrogène 4, qui se présente avantageusement sous la forme d'un dispositif de type PSA (« Pressure swing adsorption ») également largement décrit  
35       dans la littérature et notamment par le brevet FR 2.890.655 de l'Air Liquide.

Finalement, comme le montre la figure 1, et conformément aux dispositions avantageuses de l'invention, on obtient en sortie du PSA 4 un gaz hydrogène 8 quasiment pur, dont une partie 9 est prélevée et envoyée comme combustible vers le four du vaporéformeur 20. Ainsi, les effluents de cheminée 14 du vaporéformeur 20 sont exempts de CO<sub>2</sub> en marche continue du vaporéformeur 20. L'hydrogène ajouté en amont dans la charge 1 pour son hydrodésulfuration 2 et/ou 5 est également prélevé de façon classique sur le flux 8. Au démarrage cependant, de manière transitoire comme déjà explicité, les brûleurs du four seront alimentés par un combustible annexe autre que l'hydrogène, par exemple par du gaz naturel.

Egalement, de manière préférée, on recycle la purge 10 (issue de l'unité de séparation et de purification 4 de l'hydrogène) riche en méthane, hydrogène, CO et CO<sub>2</sub> résiduels, après relevage en pression 12 approprié, en tant que charge additionnelle à la charge initiale 1.

On va maintenant décrire en référence à la Figure 2, une variante de réalisation de l'invention, c'est-à-dire un procédé de production d'hydrogène par réformage autotherme et synthèse de type Fischer-Tropsch, à partir de gaz naturel.

A la figure 2, un flux de gaz naturel 1', après prétraitement usuel de type hydrodésulfuration 3' et pré-réformage 4', puis passage dans un train d'échange de chaleur 2'a, alimente un four de type autotherme 2'. Ce type de four est par exemple décrit dans le brevet FR 2.904.830 de l'IFP, déjà cité plus haut en référence à la figure 1. Dans un tel four on réalise une oxydation partielle de la charge de gaz naturel 1' (voir flux d'oxygène 5' à la figure 2), immédiatement suivie par un vaporéformage catalytique en régime adiabatique à haute température, par exemple dans la plage de températures de sortie : 900°C-1000°C.

Ce train d'échange de chaleur 2'a correspond à la zone de combustion du four autotherme 2', représentée artificiellement de manière séparée du four 2' sur la figure 2. Cette zone de combustion est alimentée en air de combustion 19' et en gaz naturel 1' au démarrage puis en hydrogène 10'b. Les fumées sont évacuées par la cheminée 14'.

D'autres éléments techniques relatifs au procédé de réformage autotherme peuvent être trouvés dans l'ouvrage de référence « Conversion processes » (procédés de conversion), P. Leprince, Editions Technip, 2001, Paris 15<sup>ème</sup>, pages 455-495.

5           Le gaz de synthèse 6' produit par le four autotherme 2' est refroidi par utilisation d'un système complexe 20' mais standard alliant récupération de chaleur, production de vapeur et train de refroidissement. Le flux gazeux 7' traité en 20', traverse ensuite un  
10           dispositif de « water gas shift » 8' (déjà décrit plus haut en préambule et en référence à la figure 1) permettant d'en ajuster le rapport  $H_2/CO$  en vue de son traitement ultérieur.

          La fraction gazeuse issue du « water gas shift » 8' est, comme dans l'exemple de réalisation de la figure 1, envoyée dans une unité de  
15           séparation du dioxyde de carbone 9' au moyen de laquelle le  $CO_2$  éliminé pourra ensuite être dirigé vers des moyens de captation ou de stockage appropriés 9'a, par exemple un système de séquestration géologique. Ces moyens, qui ne font pas partie de l'invention à proprement parler, sont connus de l'homme du métier et ne sont donc pas détaillés dans la présente description.

20           Le gaz de synthèse quittant l'unité de séparation de  $CO_2$ , 9', traverse ensuite une unité de séparation et de purification d'hydrogène 10', qui se présente avantageusement sous la forme d'un dispositif de type PSA (« Pressure swing adsorption ») également largement décrit dans la littérature et notamment par le brevet FR 2.890.655 de l'Air  
25           Liquide.

          Dans une variante de réalisation, l'unité de purification d'hydrogène peut se présenter sous forme d'un système membranaire, par exemple de type « Medal<sup>TM</sup> » (« Membrane Systems DuPont Air Liquide ») fabriqué et commercialisé par la société Air Liquide. La mise  
30           en œuvre d'un tel système est aussi bien connue de l'homme du métier, et toutes les informations nécessaires peuvent être obtenues auprès de l'Air Liquide et sur son site Internet.

          Finalement, comme le montre la figure 2, et conformément aux dispositions avantageuses de l'invention, on obtient en sortie du  
35           module de purification 10', un gaz de synthèse très riche en hydrogène 10a', voire quasiment pur, dont une partie 10'b est envoyée pour combustion vers les brûleurs du four 2'a en 13'. Ainsi les effluents de



cheminée 14' du four 2'a sont exempts de CO<sub>2</sub> en marche continue de ce four.

5           Egalement, de manière préférée selon la présente invention, on recycle la purge 10'c riche en méthane et autres hydrocarbures du module de purification 10', après relevage en pression 12' approprié, en tant que charge additionnelle à la charge initiale de gaz naturel 1'.

10           Accessoirement, selon une variante de réalisation, une partie 9'b du CO<sub>2</sub> séparé en 9', après relevage en pression approprié en 15', peut être recyclée en amont du procédé en complément de la charge de gaz naturel 1', pour contribuer à l'oxydation de celle-ci qui est nécessaire au bon fonctionnement du four autotherme 2'.

15           Dans l'exemple de réalisation décrit à la figure 2, l'invention prévoit ensuite la transformation ultérieure en 16' du gaz de synthèse 10'd, après ajustement adéquat de son rapport H<sub>2</sub>/CO au moyen de la ligne de bypass 17', en hydrocarbures liquides par synthèse chimique selon divers procédés connus, par exemple usuellement le procédé dit « Fischer-Tropsch », développé en particulier par la compagnie sud-africaine Sasol, mais aujourd'hui dans le domaine public, et pour lequel un rapport H<sub>2</sub>/CO d'environ 2 en entrée est nécessaire. Les  
20           produits non intéressants 18', typiquement les coupes hydrocarbures très légères et monoxyde ou dioxyde de carbone résiduels, issus de l'étape FT 16' sont, après séparation, recyclés en amont dans le procédé.

25           L'invention qui vient d'être décrite par la Demanderesse, en proposant de manière surprenante d'alimenter la combustion d'un four de type SMR ou autotherme au moyen d'hydrogène auto-produit, résout avantageusement les difficultés techniques et économiques rencontrées couramment pour l'élimination du CO<sub>2</sub> présent dans les fumées de ce type de four.

30           Dans un schéma particulier de raffinerie visant à réduire très fortement les émissions de gaz à effet de serre, elle pourrait constituer un moyen original de centraliser en un point unique la transformation en hydrogène des combustibles habituellement utilisées, cet hydrogène étant alors utilisé comme nouveau combustible dans les fours et  
35           chaudières, et la séparation de flux de CO<sub>2</sub> produits par la raffinerie, en construisant un SMR fonctionnant conformément à l'invention et

dédié à ladite séparation. Ce concept peut être étendu à d'autres industries utilisatrices de combustibles dans des fours ou chaudières.

REVENDEICATIONS

- 1- Procédé de fabrication d'un gaz de synthèse contenant de l'hydrogène, à partir d'une charge hydrocarbonée (1, 1'), comprenant :
- 5       - la transformation de la charge hydrocarbonée (1, 1') en gaz de synthèse contenant de l'hydrogène dans un four de type vaporéformage (20) ou de type réformage autotherme (2') ou analogue,
- 10       - le traitement du gaz de synthèse par des moyens de traitement pour la séparation et/ou purification de l'hydrogène contenu dans le gaz de synthèse,
- caractérisé en ce qu'une partie au moins de l'hydrogène (9, 10'b) ainsi produit est prélevée et renvoyée en amont du procédé pour alimenter la combustion dudit four (20, 2').
- 15       2- Procédé selon la revendication 1, dans lequel au moins une partie du flux gazeux hydrocarboné issu des moyens de traitement et/ou de la transformation de la charge en gaz de synthèse, est prélevée et recyclée en amont du procédé comme charge hydrocarbonée additionnelle du four (10,
- 20       10'c).
- 25       3- Procédé selon l'une quelconque des revendications 1 à 2, dans lequel le traitement du gaz de synthèse contenant de l'hydrogène comprend l'élimination du CO<sub>2</sub> au moyen d'une unité de séparation du dioxyde de carbone (6, 9').
- 30       4- Procédé selon la revendication 3, dans lequel le dioxyde de carbone formé est partiellement utilisé comme agent oxydant du procédé dans le four de réformage.
- 35       5- Procédé selon l'une des revendications 3 ou 4, caractérisé en ce que l'unité de séparation du dioxyde de carbone est du type mettant en œuvre des solvants chimiques, type amines ou équivalents.

- 6- Procédé selon l'une des revendications 3 ou 4, caractérisé en ce que l'unité de séparation du dioxyde de carbone est du type mettant en œuvre le procédé dit « Benfield ».
- 5 7- Procédé selon l'une des revendications 3 ou 4, caractérisé en ce que l'unité de séparation du dioxyde de carbone est du type mettant en œuvre des solvants physiques.
- 10 8- Procédé selon l'une des revendications 3 ou 4, caractérisé en ce que l'unité de séparation du dioxyde de carbone est du type mettant en œuvre des séparations par moyens physiques du type tamis moléculaires ou du type à membrane.
- 15 9- Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que les moyens de traitement comprennent une unité de séparation et de purification d'hydrogène (4, 10').
- 20 10- Procédé selon la revendication 9, caractérisé en ce que l'unité de séparation et de purification d'hydrogène est un dispositif de type PSA (« Pressure swing adsorption »).
- 25 11- Procédé selon la revendication 9, caractérisé en ce que l'unité de séparation et de purification d'hydrogène est un dispositif de type à membrane.
- 30 12- Procédé selon l'une des revendications 9 à 11, caractérisé en ce que tout ou partie d'un gaz de purge (10, 10') de l'unité de séparation et de purification d'hydrogène est recyclée en amont du procédé comme charge hydrocarbonée additionnelle.
- 35 13- Procédé selon l'une des revendications précédentes, caractérisé en ce qu'on récupère la chaleur des fumées à base de vapeur d'eau produites par la combustion de l'hydrogène dans le four, pour le préchauffage de la charge

hydrocarbonée d'alimentation du four et/ou pour le préchauffage de l'eau de chaudière de l'étape de transformation de la charge hydrocarbonée en gaz de synthèse.

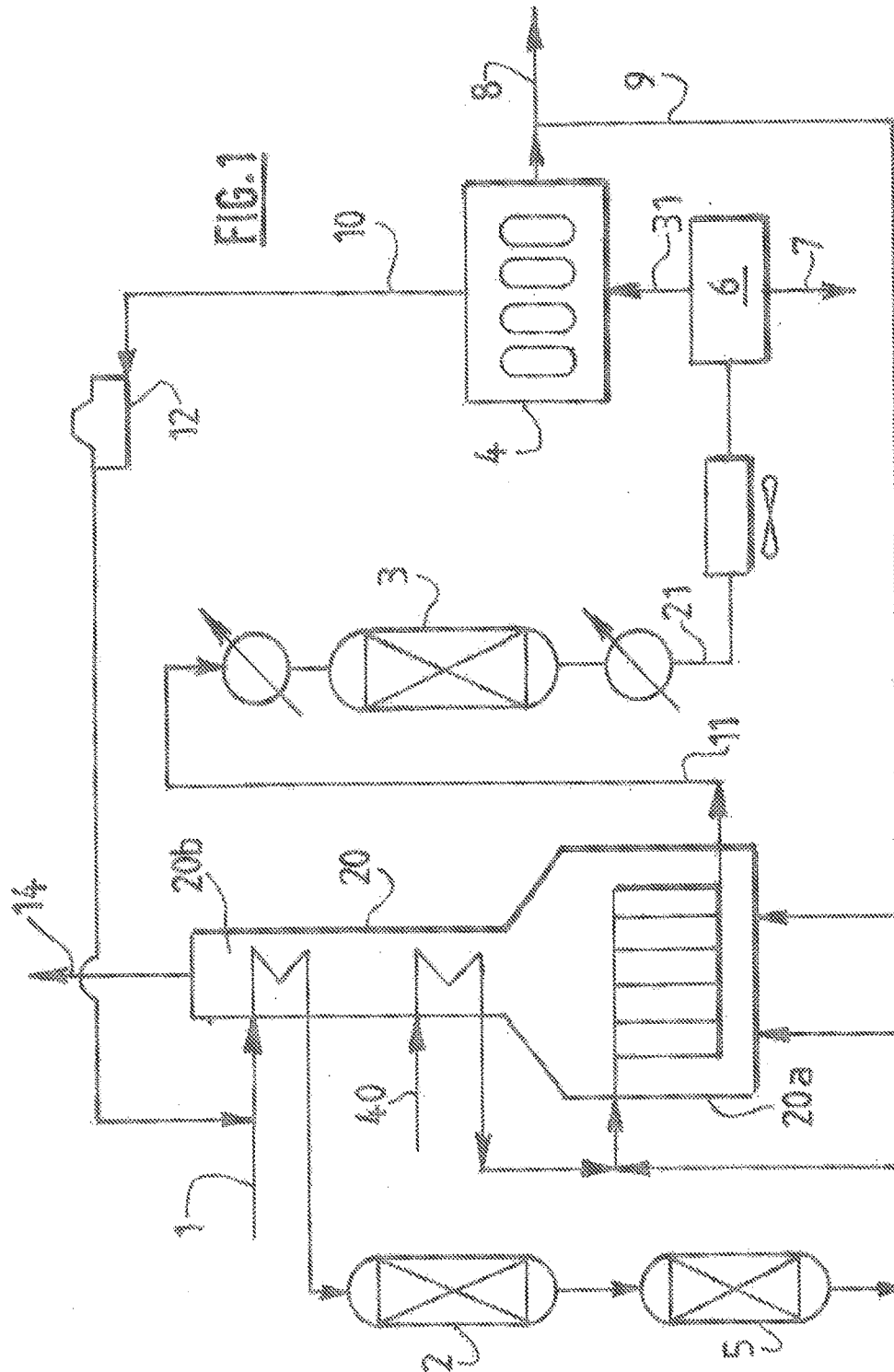
- 5
- 14- Procédé selon la revendication 13, dans lequel la chaleur est récupérée jusqu'à condensation partielle ou totale de la vapeur d'eau contenue dans les fumées.
- 10
- 15- Procédé selon l'une des revendications 1 à 14 dans lequel la charge hydrocarbonée est du méthane et le four est un four à vaporéformage, le méthane subissant un réformage à la vapeur.
- 15
- 16- Procédé selon l'une des revendications 1 à 14, dans lequel la charge hydrocarbonée est du méthane ou du naphta, et le four est un four autotherme, la charge hydrocarbonée subissant un réformage autotherme.
- 20
- 17- Procédé selon l'une des revendications 1 à 14, dans lequel la charge hydrocarbonée est du gaz naturel, le four est un four de vaporéformage, et dans lequel une autre partie de l'hydrogène ainsi produit est prélevée et renvoyée à l'alimentation d'une turbine à gaz.
- 25
- 18- Procédé selon l'une des revendications 1 à 14 dans lequel la charge hydrocarbonée est un hydrocarbure gazeux ou liquide, et dans lequel une autre partie de l'hydrogène ainsi produit est prélevée et renvoyée comme combustible pour
- 30
- un ou plusieurs fours et/ou chaudières de l'industrie utilisatrice de combustibles pour satisfaire ses besoins énergétiques.
- 35
- 19- Procédé selon la revendication 18 dans lequel la charge hydrocarbonée est un fuel gaz ou hydrocarbure liquide provenant d'une unité d'une raffinerie ou du gaz naturel, et dans lequel une autre partie de l'hydrogène ainsi produit est

prélevée et renvoyée comme combustible pour un ou plusieurs fours et/ou chaudières de la raffinerie.

- 5            20-    Procédé selon l'une des revendications 1 à 19 dans lequel les produits non recherchés, après l'étape de finale de transformation du gaz de synthèse en produits commercialisables, sont séparés et recyclés dans le procédé de réformage amont.

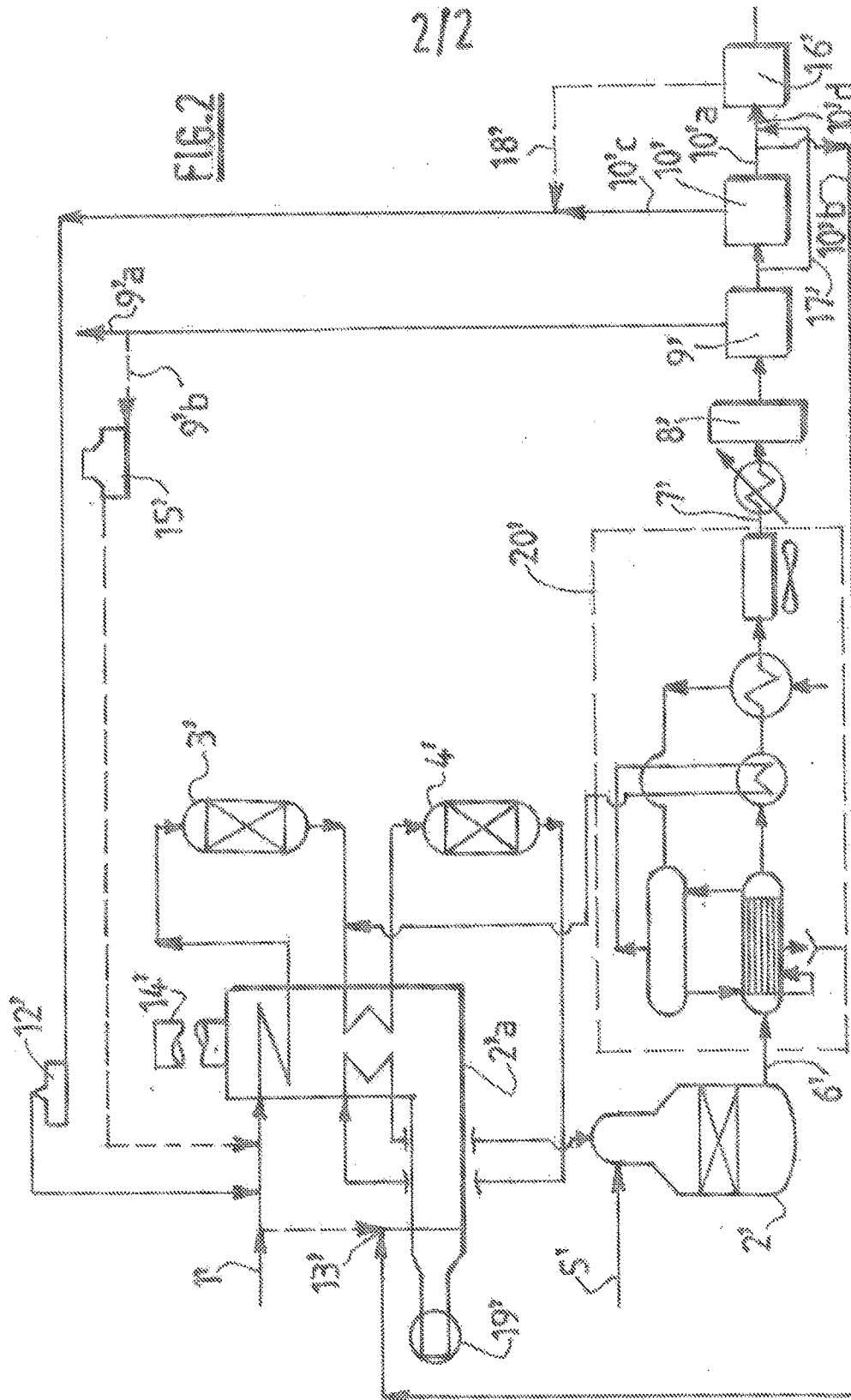
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FIG. 2







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FR 0956030

| DOCUMENTS CONSIDÉRÉS COMME PERTINENTS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                                                              | Revendication(s)<br>concernée(s) | Classement attribué<br>à l'invention par l'INPI |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|-------------------------------------------------|
| Catégorie                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Citation du document avec indication, en cas de besoin,<br>des parties pertinentes                                                                                                                                                                                                                                           |                                  |                                                 |
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| -----<br>-/--<br>-----                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                                                                                                              |                                  |                                                 |
| Date d'achèvement de la recherche                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                                                                                              | Examineur                        |                                                 |
| 19 avril 2010                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                              | Engelen, Karen                   |                                                 |
| <p>CATÉGORIE DES DOCUMENTS CITÉS</p> <p>X : particulièrement pertinent à lui seul<br/>Y : particulièrement pertinent en combinaison avec un autre document de la même catégorie<br/>A : arrière-plan technologique<br/>O : divulgation non-écrite<br/>P : document intercalaire</p> <p>T : théorie ou principe à la base de l'invention<br/>E : document de brevet bénéficiant d'une date antérieure à la date de dépôt et qui n'a été publié qu'à cette date de dépôt ou qu'à une date postérieure.<br/>D : cité dans la demande<br/>L : cité pour d'autres raisons<br/>&amp; : membre de la même famille, document correspondant</p> |                                                                                                                                                                                                                                                                                                                              |                                  |                                                 |

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établi sur la base des dernières revendications  
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national

FA 728362  
FR 0956030

| DOCUMENTS CONSIDÉRÉS COMME PERTINENTS                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                                                                   | Revendication(s)<br>concernée(s)                                                                                                                                                                                                                                                                                                          | Classement attribué<br>à l'invention par l'INPI |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| Catégorie                                                                                                                                                                                                                              | Citation du document avec indication, en cas de besoin,<br>des parties pertinentes                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                                                                           |                                                 |
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| E                                                                                                                                                                                                                                      | -----<br>EP 2 168 913 A1 (INST FRANCAIS DU PETROLE<br>[FR]) 31 mars 2010 (2010-03-31)<br><br>* alinéa [0026] - alinéa [0031]; figure 3<br>*                                                                                                                                                                       | 1-5,9,<br>12,15,<br>17,20                                                                                                                                                                                                                                                                                                                 | DOMAINES TECHNIQUES<br>RECHERCHÉS (IPC)         |
| Date d'achèvement de la recherche                                                                                                                                                                                                      |                                                                                                                                                                                                                                                                                                                   | Examineur                                                                                                                                                                                                                                                                                                                                 |                                                 |
| 19 avril 2010                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                   | Engelen, Karen                                                                                                                                                                                                                                                                                                                            |                                                 |
| CATÉGORIE DES DOCUMENTS CITÉS                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                   | T : théorie ou principe à la base de l'invention<br>E : document de brevet bénéficiant d'une date antérieure<br>à la date de dépôt et qui n'a été publié qu'à cette date<br>de dépôt ou qu'à une date postérieure.<br>D : cité dans la demande<br>L : cité pour d'autres raisons<br>& : membre de la même famille, document correspondant |                                                 |
| X : particulièrement pertinent à lui seul<br>Y : particulièrement pertinent en combinaison avec un<br>autre document de la même catégorie<br>A : arrière-plan technologique<br>O : divulgation non-écrite<br>P : document intercalaire |                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                           |                                                 |

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**ANNEXE AU RAPPORT DE RECHERCHE PRÉLIMINAIRE  
RELATIF A LA DEMANDE DE BREVET FRANÇAIS NO. FR 0956030 FA 728362**

La présente annexe indique les membres de la famille de brevets relatifs aux documents brevets cités dans le rapport de recherche préliminaire visé ci-dessus.

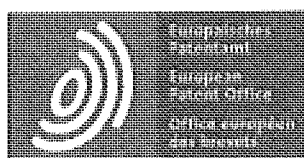
Les dits membres sont contenus au fichier informatique de l'Office européen des brevets à la date du 19-04-2010

Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office européen des brevets, ni de l'Administration française

| Document brevet cité<br>au rapport de recherche | Date de<br>publication | Membre(s) de la<br>famille de brevet(s) | Date de<br>publication |
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Espacenet

FR2949772A1 Producing a synthesis gas containing hydrogen from a hydrocarbon charge including e.g. methane or naphtha, comprises transforming hydrocarbon charge into synthesis gas in vapor-reforming furnace, and treating the synthesis gas

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Producing a synthesis gas containing hydrogen from a hydrocarbon charge including e.g. methane or naphtha, comprises transforming hydrocarbon charge into synthesis gas in vapor-reforming furnace, and treating the synthesis gas

## Abstract

The process of producing a synthesis gas containing hydrogen from a hydrocarbon charge (1), comprises transforming the hydrocarbon charge into synthesis gas in a vapor-reforming furnace or auto-thermal reforming furnace, and treating the synthesis gas using a unit (4) for separation and/or purification of hydrogen. The hydrogen product is removed and supplied in upstream of the furnace for performing combustion. A part of hydrocarbon gas flow obtained from the treatment unit and/or transformation of synthesis gas is removed and recycled in upstream of the process. The process of producing a synthesis gas containing hydrogen from a hydrocarbon charge (1), comprises transforming the hydrocarbon charge into synthesis gas in a vapor-reforming furnace or auto-thermal reforming furnace, and treating the synthesis gas using a unit (4) for separation and/or purification of hydrogen. The hydrogen product is removed and supplied in upstream of the furnace for performing combustion. A part of hydrocarbon gas flow obtained from the treatment unit and/or transformation of synthesis gas is removed and recycled in upstream of the process as additional hydrocarbon load for the furnace. The step of treatment of synthesis gas comprises a step of elimination of carbon dioxide using a separation unit, where the carbon dioxide is used as an oxidizing agent in the reforming furnace. The carbon dioxide separation unit comprises chemical solvents including amines and physical solvents, and is capable of performing Benfield process and physical separation using molecular sieve or membrane. The treatment unit for separation and/or purification of hydrogen is a device of pressure swing adsorption type or membrane type. The purge gas from the hydrogen separation and purification unit is recycled in upstream of process as additional hydrocarbon charge. The process further comprises recovering heat from the smoke based on water vapor produced by the combustion of hydrogen in the furnace to preheat the hydrocarbon feedstock supply in the furnace and/or to preheat hot water during the hydrocarbon processing stage. The heat is recovered until partial or total condensation of water vapor contained in the smoke.





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### DESCRIPTION FR2949772A1

□

#### METHOD FOR MANUFACTURING A SYNTHESIS GAS OR HYDROGEN, FROM A HYDROCARBON CHARGER

The invention relates to a method for producing a synthesis gas or hydrogen, from a hydrocarbon feedstock or the like, in which the hydrocarbon feedstock is converted mainly into synthesis gas or hydrogen in a steam reforming or of the autothermal reforming type or the like, in which the gas stream thus produced is treated in order to eliminate the carbon dioxide therefrom and to purify the hydrogen content therein, in which part of the hydrogen obtained at the output of the stages mentioned above, is used upstream of the process to feed the combustion of said furnace. Optionally and advantageously, a gaseous stream rich in hydrocarbon or carbon monoxide resulting from the means of separation and purification of said gaseous stream produced in the process downstream of the furnace outlet, is recycled upstream of the process as additional hydrocarbon feedstock.

The invention lies more particularly in the field of the production of synthesis gas or hydrogen from a hydrocarbon feedstock, using for example a furnace of the vapor reforming type (known for a methane hydrocarbon feedstock under the acronym SMR which comes from the English ♦ steam methane reforming ♦ which means ♦ steam methane reforming ♦) or so-called autothermal reforming (known by the acronym ATR which comes from the English ♦ autothermal reformer ♦ which means autothermal reformer, or autothermal ), the heat of combustion of which is generally produced by burning a hydrocarbon type fuel.

The main object of the invention is to reduce the carbon dioxide (CO<sub>2</sub>) content in the fumes from the furnace as much as possible by using hydrogen produced in the process as fuel. Indeed, these fumes which have a low CO<sub>2</sub> partial pressure and which also contain other gases such as oxygen, water vapor and nitrogen, are not easy to treat. On this subject, reference can be made to the publication entitled "Post-combustion capture of CO<sub>2</sub>" by Sulzer Chemtech published in the journal PTQ (Q2-2009).

Another object of the invention is to provide a device for separating the carbon dioxide resulting from the process for producing synthesis gas with a view to subsequent separate sequestration. As already mentioned above, for the professional engineer who seeks to eliminate the CO<sub>2</sub> produced in a process, for example the manufacture of a synthesis gas, the most obvious solution is to try to capture the CO<sub>2</sub> present in the part of the process which operates at higher pressure, i.e. where the main gas flow produced in the process circulates. However, this gas flow represents only a part (typically of the order of 55% by weight in an SMR unit with methane charge), even if it is not negligible, of the CO<sub>2</sub> generated in the process. The rest of the CO<sub>2</sub> (approximately 45% by weight) is emitted by the fumes from the furnace for which the existing treatment methods are difficult to implement given the low pressure of the fumes and the large volumes of gas to be treated.

This requires in particular to significantly increase the pressure of large volumes of gas, and consequently, the person skilled in the art only rarely plans to capture the CO<sub>2</sub> generated at the level of the fumes from the furnace because the cost of the operation turns out to be excessively high.

The invention proposed by the Applicant enables almost total capture of the CO<sub>2</sub> which can be produced in the process. It is mainly characterized by the fact that, surprisingly, part of the hydrogen produced in the process is taken in order to use it as fuel

for the hydrogen or synthesis gas production furnace. This provision may seem surprising because hydrogen is expensive, but the Applicant has demonstrated on examples that the net production of hydrogen or synthesis gas is little affected by this use of hydrogen in the furnace, because the type fuel gas which is thus saved instead of being burned in the furnace, can be used as an additional charge for the process and consequently be transformed into hydrogen. This saved fuel-gas thus itself becomes an additional source of hydrogen. Processes for producing synthesis gas and hydrogen are already known. For example, US Pat. No. 7,405,243 from CHEVRON describes a process for the synthesis of hydrocarbons, for example of the Fischer-Tropsch type, making it possible to obtain, with other hydrocarbon cuts, after treatment, a hydrogen of high purity.

This invention contemplates several possible uses for this hydrogen, for example in various processes for the hydrotreating of hydrocarbon products or the rejuvenation of catalysts.

The invention described by patent FR 2,890,655 of Air Liquide, relates to a process for converting hydrocarbon gases into hydrocarbon liquids in which the following are implemented: - in a first step, the conversion of the hydrocarbon gases into synthesis gas, - in a second stage, the Fischer-Tropsch process producing a residual gas containing hydrogen, - in a third stage, a hydrocracking by means of a hydrogenated gas, in which the hydrogenated gas is produced by a purification process PSA of waste gas from the Fischer-Tropsch process and of a gaseous effluent rich in hydrogen from a steam methane reforming unit. However, although falling within the scope of the present invention, neither of the two aforementioned references describes or suggests the characteristics of the invention, and in particular the use of hydrogen to fuel a combustion of an SMR furnace or the like. The present invention, consisting in using pure hydrogen as furnace fuel and, in an advantageous variant, in recycling certain separation purge streams as additional hydrocarbon feedstock upstream of the process, thus makes it possible to eliminate the presence of CO<sub>2</sub> in furnace fumes and thereby limit the problem of CO<sub>2</sub> capture to a limited number of process streams, which operate at relatively high pressure.

A suitable separation module installed on the main flow of the syngas will allow the extraction of the CO<sub>2</sub> with a view to a separate capture of the CO<sub>2</sub> which can then be recovered in an appropriate manner. The technological options thus retained may generate some disadvantages such as the slight oversizing of the SMR unit and the corresponding moderate overinvestment, but this is worth the price to pay for the almost complete capture of CO<sub>2</sub> in the process. Controlling the combustion of hydrogen also requires certain precautions, the calorific value of hydrogen being lower than that of the hydrocarbons usually used. In the start-up phase of the furnace, unless you have stored hydrogen, you will have to burn another fuel and emit CO<sub>2</sub>. During this transitional phase, this auxiliary fuel will be used until the moment when the production of hydrogen is well established, and will thus authorize switching the supply of the burners of the furnace to hydrogen.

This same auxiliary fuel can be used in certain transitional phases during which the production of hydrogen would become momentarily insufficient, such as for example during an unexpected triggering of a downstream hydrogen flow separation purification unit. Thus the present invention describes a method for producing a synthesis gas or hydrogen, from a hydrocarbon feed or the like, in which the hydrocarbon feed is transformed into synthesis gas containing hydrogen in a vapor reforming type or autothermal reforming type or the like, in which the synthesis gas is treated by treatment means for the separation and/or purification of the hydrogen contained in the synthesis gas, characterized in that at least part hydrogen thus produced is withdrawn and returned upstream of the process to supply the combustion of said furnace. Optionally and advantageously, at least a part of the hydrocarbon gas stream resulting from the means for processing and/or converting the feedstock into synthesis gas, this stream being in particular a gas stream rich in hydrocarbon or carbon monoxide, is withdrawn and recycled upstream of the process as additional hydrocarbon feedstock for the process.

The means for processing the synthesis gas forming the main gas stream include a reactor for converting CO to steam (or "water gas shift" in English, the expression most often used), a carbon dioxide separation unit and a hydrogen separation and purification unit. A "water gas shift" is a unit known to those skilled in the art, which makes it possible to reduce the CO content of the treated gas and to increase its hydrogen content (by carrying out the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ) until an H<sub>2</sub>/CO ratio is obtained in the treated gas-which is suitable for subsequent transformation of this synthesis gas into liquid hydrocarbons by chemical synthesis according to various known processes (for example the Fischer-Tropsch process for which a H<sub>2</sub>/CO ratio close to 2 is necessary). The carbon dioxide separation unit allows the separation of CO<sub>2</sub> for subsequent capture. Advantageously, the carbon dioxide formed can be partially used as the oxidizing agent of the process in the reforming furnace, that is to say that part of this carbon dioxide formed is returned as an oxidant, or as d In other words, CO<sub>2</sub> is returned to the furnace as an oxidizing agent in addition to another oxidizing agent, which is either steam for the SMR or oxygen for the autothermal furnace.

This carbon dioxide separation unit can be of the type using chemical solvents, amine type or equivalent. According to a preferred embodiment of the invention, the carbon dioxide separation unit is of the type implementing the so-called

"Benfield" process, well known to those skilled in the art. The carbon dioxide separation unit can also be of the type using physical solvents, of the "Rectisol" type or the like. The carbon dioxide separation unit can also be of the type implementing separations by physical means of the molecular sieve type or of the membrane type.

Other processes can be implemented, such as for example the "Econamine FG" process marketed by the American engineering company Fluor Daniel, or units operating cryogenically. The carbon dioxide separation unit installed on the main process stream can be located upstream or downstream of the PSA unit mentioned above according to the processes implemented and according to the technical and economic optimization considerations retained. According to an advantageous feature of the invention, all or part of a purge gas from the hydrogen separation and purification unit is recycled upstream of the process as additional hydrocarbon feedstock. According to a preferred embodiment of the invention, in the case of a unit aimed at producing essentially hydrogen (as will be described later in the description in FIG. 1), the separation and purification unit of Hydrogen is of the PSA (Pressure Swing Adsorption) type.

The purge gas from such a PSA unit then contains carbon monoxide, carbon dioxide, as well as residual hydrogen and methane. By thus recycling in the charge molecules of the CH<sub>4</sub> type in particular which are not directly recoverable in the state downstream of the process, the loss of hydrogen which is used in the combustion of the furnace is partially compensated.

According to another preferred embodiment of the invention, in the case of a unit aimed at producing essentially a synthesis gas to supply a Fischer Tropsch unit as described below in detail in FIG. 2, or for a unit methanol synthesis or other similar applications; the hydrogen separation and purification unit is of the membrane type making it possible to sample the quantity of hydrogen (in low-pressure flow at the membrane outlet) necessary to supply the furnace. The hydrogen separation and purification unit is for example of the membrane type of the  $\diamond$ Medal $\diamond$  type. The pressure regulation loops, making it possible to ensure the withdrawal of the necessary quantity of hydrogen and the obtaining of the correct H<sub>2</sub>/CO ratio in the main flow, will be set up for this purpose without particular difficulty according to the rules of the skilled in the art.

In the case of a synthesis gas production unit, the flow recycled in the feedstock of the reforming unit will preferably consist of the residual molecules of carbon monoxide and dioxide, hydrogen and methane coming out of the synthesis step after separation of the desired products (C<sub>5</sub>+ hydrocarbon, or methanol, or heavy alcohols). However, the hydrogen separation and purification unit can also be of the PSA type. Furthermore, the use of hydrogen as fuel for the furnace provides an opportunity to improve the useful efficiency of the furnace.

Thus, according to another preferred embodiment of the invention, it is possible to recover the heat from the fumes based on water vapor produced by the combustion of hydrogen in the furnace, for example by condensation of the water vapor present in the fumes from the furnace, for the preheating of process boiler water and/or preferably for the preheating of the hydrocarbon feedstock of the furnace. This increases the operating efficiency of the furnace and more marginally (by a few percent) the production efficiency of the final product gas. In particular, the heat can be recovered until partial or total condensation of the water vapor contained in the flue gases. The hydrocarbon feed of the process according to the invention may be methane and the furnace may be a steam reforming furnace, the methane undergoing steam reforming. As a variant, the hydrocarbon charge of the process according to the invention can be methane or naphtha, and the furnace can be an autothermal furnace, the hydrocarbon charge undergoing autothermal reforming.

In the case of an implementation upstream of a gas turbine or "TAG", an SMR operating on natural gas producing hydrogen according to the proposed invention, would make it possible to supply the TAG with hydrogen for combustion, the CO<sub>2</sub> discharge being channeled next to the SMR, upstream of the TAG. This is probably one of the few conceivable solutions for having a TAG integrating a complete capture of the associated CO<sub>2</sub> and applicable to other gaseous or gaseous fossil fuels. We can also advantageously cite the example of a refinery which would tackle the capture of CO<sub>2</sub> with a view to subsequent sequestration, and which, according to the inventive solution described, could for this purpose install a dedicated SMR to centrally transform and with a view to maximizing the quantities captured, the furnace fuels (fuel-gas produced by the refinery units, additional natural gas, or even a liquid hydrocarbon fuel, for example a gasoline or diesel cut), in hydrogen instead of send directly for combustion in refinery furnaces and/or boilers.

The main benefit is to achieve a separation of CO<sub>2</sub> in this way at a single determined point instead of multiplying the separation points corresponding to several dozen furnaces or boilers for a conventional refinery, making it possible to solve the previously described difficulty of achieving a smoke capture.

Since steam reforming itself is a net steam producer in certain process configurations, such a solution could advantageously partially replace a boiler capacity to be built, which can contribute to justifying more easily the economic implementation of the scheme thus adopted. Following the same principle, any industry using gas (self-produced or



natural gas imported into its enclosure) in furnaces or boilers, such as the steel industry, can apply the same type of solution. In the preceding examples, it will be appropriate, as described previously, to take advantage, if possible, of the condensation of the water vapors in the flue gases from the furnace to increase the thermal yields of the heat-using units. Advantageously, the undesired products, after the final stage of transformation of the synthesis gas into marketable products, will be separated and recycled in the upstream reforming process.

The invention is now described with reference to the appended, non-limiting drawings, in which: FIG. 1 is a block diagram of a process according to the invention, illustrating the application to the production of hydrogen by steam reforming of methane; - Figure 2 is a block diagram of a process variant according to the invention, illustrating the application to the production of hydrogen by autothermal reforming and Fischer-Tropsch type synthesis.

In the installation of FIG. 1, the hydrocarbon charge 1 (methane or natural gas in this case) is preheated by heat exchange in the upper part 20b of the methane vapor reformer 20, generally called the convection section. This type of steam reformer is well known to those skilled in the art. For example, patent FR 2,904,830 from IFP, cited here by way of reference, gives a detailed description thereof. Another well-known manufacturer of this type of equipment is Foster Wheeler, which markets it under the trademark ♦Terrace-WallTM♦.

The hydrocarbon charge 1, after adding hydrogen and preheating in various heat exchangers, is then pretreated in a hydrogenation reactor 2, then in a desulfurization reactor 5, before being sent to the catalytic part 20a of the steam reformer 20 where it reacts in the presence of water vapor to obtain a synthesis gas 11 which mainly contains, excluding water vapor, a mixture of carbon oxides and hydrogen.

The synthesis gas 11 is then sent to a reactor 3 for the conversion of CO to water vapor (or "water gas shift" in English, the expression most often used) which makes it possible to reduce the CO content of the treated gas and to increase its hydrogen content (by carrying out the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ). The necessary water vapor is produced essentially in the convection of the furnace from demineralised water 40 and is generally introduced into the process stream upstream of the furnace. The synthesis gas 21 thus treated is then sent to a carbon dioxide separation unit 6 by means of which the separated  $\text{CO}_2$  7 can then be directed to appropriate capture or storage means. These means, which do not form part of the invention strictly speaking, are known to those skilled in the art and are currently the subject of numerous and varied developments and experiments. An example is geological sequestration in former gas or oil reservoirs.

The carbon dioxide separation unit 6 is for example of the well-known type implementing the so-called "Benfield" process, currently licensed by the American company UOP (Honeywell Group). Other processes with the same purpose are described in the literature and reference may be made in particular to the publication entitled ♦Recovery of  $\text{CO}_2$  from Flue Gases: Commercial Trends♦, initially presented at the annual meeting of the ♦Canadian Society of Chemical Engineers♦, October 4-6, 1999, Saskatoon, Saskatchewan, Canada, by Dan G. Chapel and Cari L. Mariz of the American company Fluor Daniel. The synthesis gas 31 leaving the  $\text{CO}_2$  separation unit 6 then passes through a hydrogen separation and purification unit 4, which advantageously takes the form of a PSA (Pressure Swing Adsorption) type device. ) also widely described in the literature and in particular by patent FR 2,890,655 of Air Liquide.

Finally, as shown in Figure 1, and in accordance with the advantageous provisions of the invention, an almost pure hydrogen gas 8 is obtained at the outlet of the PSA 4, part 9 of which is taken and sent as fuel to the furnace of the steam reformer 20. Thus, the chimney effluents 14 of the steam reformer 20 are free of  $\text{CO}_2$  in continuous operation of the steam reformer 20. The hydrogen added upstream in charge 1 for its hydrodesulphurization 2 and/or 5 is also taken in the conventional manner from stream 8. On start-up, however, in a transitional manner as already explained, the burners of the furnace will be powered by an auxiliary fuel other than hydrogen, for example by natural gas. Also, preferably, the purge 10 (from the hydrogen separation and purification unit 4) rich in residual methane, hydrogen, CO and  $\text{CO}_2$  is recycled, after raising the appropriate pressure 12, as feed. additional to the initial charge 1.

Will now be described with reference to Figure 2, a variant embodiment of the invention, that is to say a process for producing hydrogen by autothermal reforming and Fischer-Tropsch type synthesis, from natural gas .

In FIG. 2, a flow of natural gas 1', after usual pretreatment of the hydrodesulfurization type 3' and pre-reforming 4', then passing through a heat exchange train 2'a, supplies an autothermal type furnace 2'. This type of furnace is for example described in patent FR 2,904,830 of IFP, already cited above with reference to Figure 1. In such a furnace, partial oxidation of the natural gas charge 1' is carried out (see oxygen flow 5' in FIG. 2), immediately followed by catalytic steam reforming in an adiabatic regime at high temperature, for example in the range of outlet temperatures: 900°C-1000°C. This heat exchange train 2'a corresponds to the combustion zone of the autothermal furnace 2',

represented artificially separately from the furnace 2' in FIG. 2. This combustion zone is supplied with combustion air 19' and with natural gas 1' at start-up then with hydrogen 10'b.

The fumes are evacuated through the chimney 14'.

Other technical elements relating to the autothermal reforming process can be found in the reference work ♦ Conversion processes ♦ (processes de conversion), P. Leprince, Editions Technip, 2001, Paris 15ème, pages 455-495.

The syngas 6' produced by the autothermal furnace 2' is cooled by using a complex but standard system 20' combining heat recovery, steam production and cooling train. The gas stream 7' treated at 20' then passes through a "water gas shift" device 8' (already described above in the preamble and with reference to FIG. 1) making it possible to adjust the H<sub>2</sub>/CO ratio with a view to its further processing. The gaseous fraction resulting from the "water gas shift" 8' is, as in the embodiment of FIG. 1, sent to a carbon dioxide separation unit 9' by means of which the CO<sub>2</sub> removed can then be directed to appropriate capture or storage means 9'a, for example a geological sequestration system. These means, which do not form part of the invention strictly speaking, are known to those skilled in the art and are therefore not detailed in the present description.

The synthesis gas leaving the CO<sub>2</sub> separation unit, 9', then passes through a hydrogen separation and purification unit 10', which advantageously takes the form of a device of the PSA type (♦ Pressure swing adsorption ♦) also widely described in the literature and in particular by Air Liquide patent FR 2,890,655. In a variant embodiment, the hydrogen purification unit may be in the form of a membrane system, for example of the "MedalTM" type (DuPont Air Liquide Membrane Systems) manufactured and marketed by the company Air Liquide. The implementation of such a system is also well known to those skilled in the art, and all the necessary information can be obtained from Air Liquide and on its website. Finally, as shown in Figure 2, and in accordance with the advantageous provisions of the invention, there is obtained at the outlet of the purification module 10', a synthesis gas very rich in hydrogen 10a', even almost pure, of which a part 10 ID is sent for combustion to the burners of the furnace 2'a at 13'.

Thus the chimney effluents 14' of the oven 2'a are free of CO<sub>2</sub> during continuous operation of this oven. Also, preferably according to the present invention, the purge 10'c rich in methane and other hydrocarbons from the purification module 10' is recycled, after raising the appropriate pressure 12', as an additional charge to the initial charge of natural gas, 1'. Incidentally, according to a variant embodiment, a part 9b of the CO<sub>2</sub> separated at 9', after raising the appropriate pressure at 15', can be recycled upstream of the process in addition to the natural gas feed 1', to contribute to the oxidation of the latter which is necessary for the proper functioning of the autothermal furnace 2'. In the exemplary embodiment described in FIG. 2, the invention then provides for the subsequent transformation into 16' of the synthesis gas 10'd, after adequate adjustment of its H<sub>2</sub>/CO ratio by means of the bypass line 17', into liquid hydrocarbons by chemical synthesis according to various known processes, for example usually the so-called "Fischer-Tropsch" process, developed in particular by the South African company Sasol, but today in the public domain, and for which an H<sub>2</sub>/CO of approximately 2 in input is required.

The non-interesting products 18', typically the very light hydrocarbon cuts and residual carbon monoxide or dioxide, resulting from the FT stage 16' are, after separation, recycled upstream in the process. The invention which has just been described by the Applicant, by surprisingly proposing to supply the combustion of an SMR or autothermal type furnace by means of self-produced hydrogen, advantageously solves the technical and economic difficulties commonly encountered for the elimination of the CO<sub>2</sub> present in the fumes of this type of oven.

In a particular refinery scheme aiming to drastically reduce greenhouse gas emissions, it could constitute an original means of centralizing at a single point the transformation into hydrogen of the fuels usually used, this hydrogen then being used as new fuel in the furnaces and boilers, and the separation of CO<sub>2</sub> streams produced by the refinery, by building an SMR operating in accordance with the invention and dedicated to said separation. This concept can be extended to other industries using fuels in furnaces or boilers.



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## CLAIMS FR2949772A1

CLAIMS 1- Process for the production of a synthesis gas containing hydrogen, from a hydrocarbon feedstock (1, 1'), comprising:  
- the transformation of the hydrocarbon feedstock (1, 1') into synthesis gas containing hydrogen in a furnace of the vapor reforming type (20) or of the autothermal reforming type (2') or the like, - the treatment of the synthesis gas by treatment means for the separation and/or purification of the hydrogen contained in the synthesis gas, characterized in that at least part of the hydrogen (9, 10'b) thus produced is withdrawn and returned upstream of the process to supply the combustion of the said furnace (20, 2').

2.

2- Process according to claim 1, in which at least a part of the hydrocarbon gas stream resulting from the means of treatment and/or from the transformation of the feedstock into synthesis gas, is taken and recycled upstream of the process as additional hydrocarbon feedstock of the furnace (10, 10'c).

3.

3- Process according to any one of claims 1 to 2, in which the treatment of the synthesis gas containing hydrogen comprises the removal of CO<sub>2</sub> by means of a carbon dioxide separation unit (6, 9').

4.

4- Process according to claim 3, in which the carbon dioxide formed is partially used as the oxidizing agent of the process in the reforming furnace.

5.

5- Method according to one of claims 3 or 4, characterized in that the carbon dioxide separation unit is of the type using chemical solvents, amine type or equivalent. 30 35

6.

6 - 57- 8- 10 15 9- 20 10- 11- 25 12- 13-35 Process according to one of Claims 3 or 4, characterized in that the carbon dioxide separation unit is of the type implementing the Benfield process. Process according to one of Claims 3 or 4, characterized in that the carbon dioxide separation unit is of the type using physical solvents. Process according to one of Claims 3 or 4, characterized in that the carbon dioxide separation unit is of the type implementing separations by physical means of the molecular sieve type or of the membrane type. Process according to any one of Claims 1 to 8, characterized in that the treatment means comprise a hydrogen separation and purification unit (4, 10'). Process according to Claim 9, characterized in that the hydrogen separation and purification unit is a device of the PSA (Pressure swing adsorption) type.

Process according to Claim 9, characterized in that the hydrogen separation and purification unit is a device of the membrane type. Process according to one of Claims 9 to 11, characterized in that all or part of a purge gas (10, 10') from the hydrogen separation and purification unit is recycled upstream of the process as additional hydrocarbon charge. Process according to one of the preceding claims, characterized in that the heat is recovered from the fumes based on water vapor produced by the combustion of hydrogen in the furnace, for preheating the hydrocarbon feedstock of the furnace and/or for preheating the boiler water from the step of transforming the hydrocarbon feedstock into synthesis gas. 14- Process according to claim 13, in which the heat is recovered until partial or total condensation of the water vapor contained in the flue gases.

10 15- Method according to one of claims 1 to 14 wherein the hydrocarbon feedstock is methane and the furnace is a steam reforming furnace, the methane undergoing steam reforming. 15 16- Method according to one of claims 1 to 14, wherein the hydrocarbon charge is methane or naphtha, and the furnace is an autothermal furnace, the hydrocarbon charge undergoing autothermal reforming. 20 17- Method according to one of claims 1 to 14, wherein the hydrocarbon charge is natural gas, the furnace is a steam reforming furnace, and wherein another part of the hydrogen thus produced is taken and returned to the feed of a gas turbine. 25 18- Method according to one of claims 1 to 14 wherein the hydrocarbon feed is a gaseous or liquid hydrocarbon, and wherein another part of the hydrogen thus produced is taken and returned as fuel for one or more furnaces and / or boilers fuel-using industry to meet its energy needs.

19- Process according to claim 18, in which the hydrocarbon feedstock is a fuel gas or liquid hydrocarbon coming from a unit of a refinery or natural gas, and in which another part of the hydrogen thus produced is withdrawn and returned as fuel for one or more refinery furnaces and/or boilers. 20- Method according to one of claims 1 to 19 wherein the undesired products, after the final stage of transformation of the synthesis gas into marketable products, are separated and recycled in the upstream reforming process. 10

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(54) Title of the Invention: Gas processing  
Abstract Title: A method of producing hydrogen

(57) A method of producing hydrogen is disclosed, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen from the feed gas; wherein the reforming processes comprise both a gas-heated reforming process (1) and an autothermal reforming process (2): and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process. Input gases to the process and the hydrogen produced may come from or be utilised in related processing plants such as a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air separation plant and a petrochemical plant.

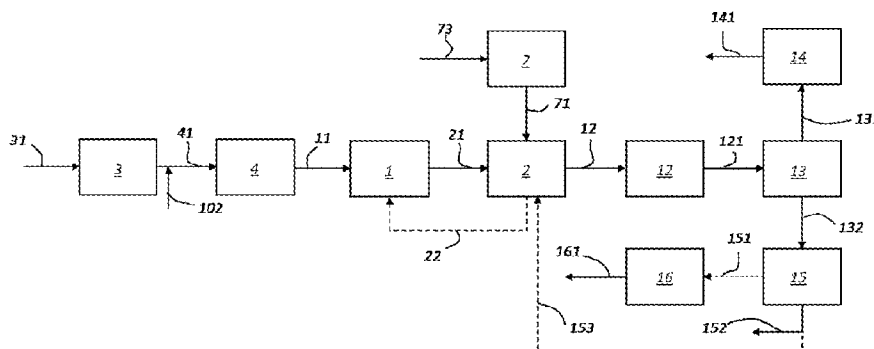


Figure 3

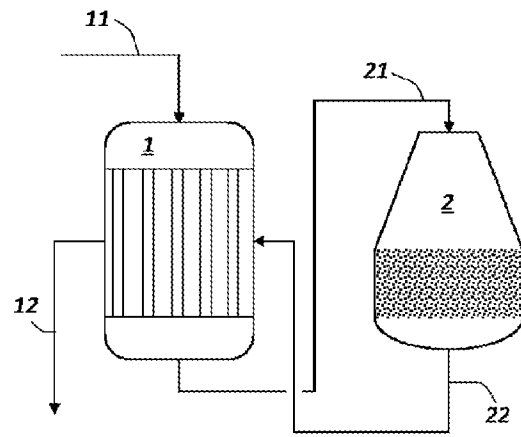


Figure 1

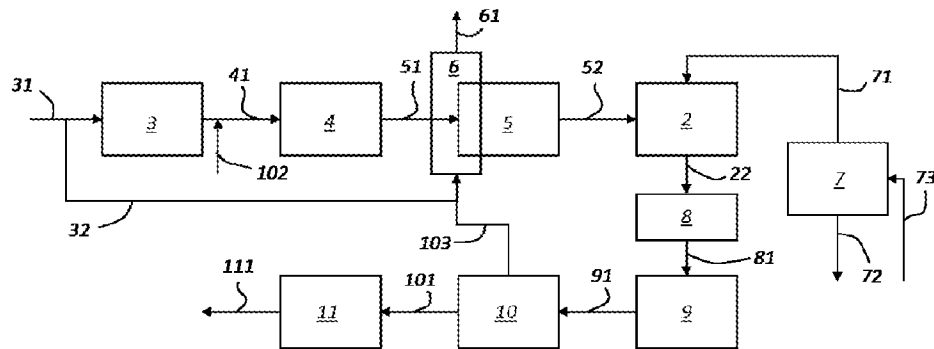


Figure 2

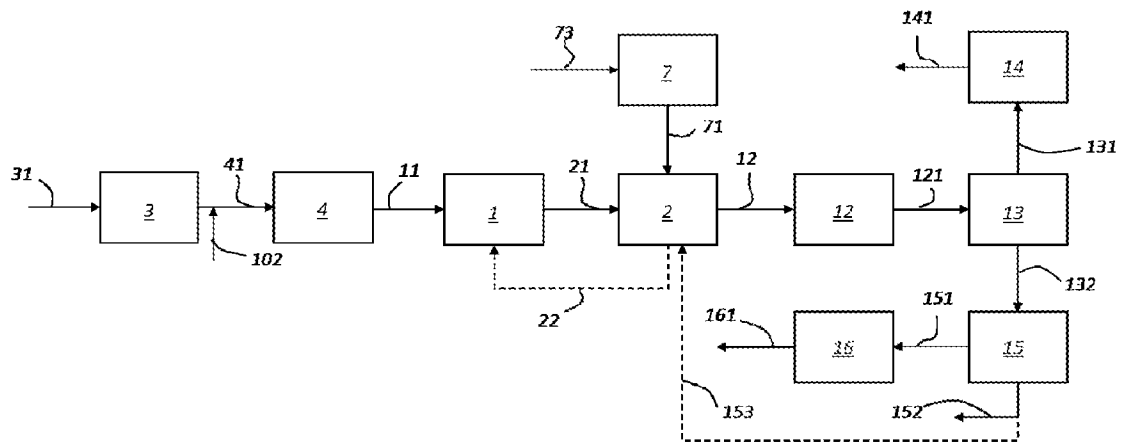


Figure 3

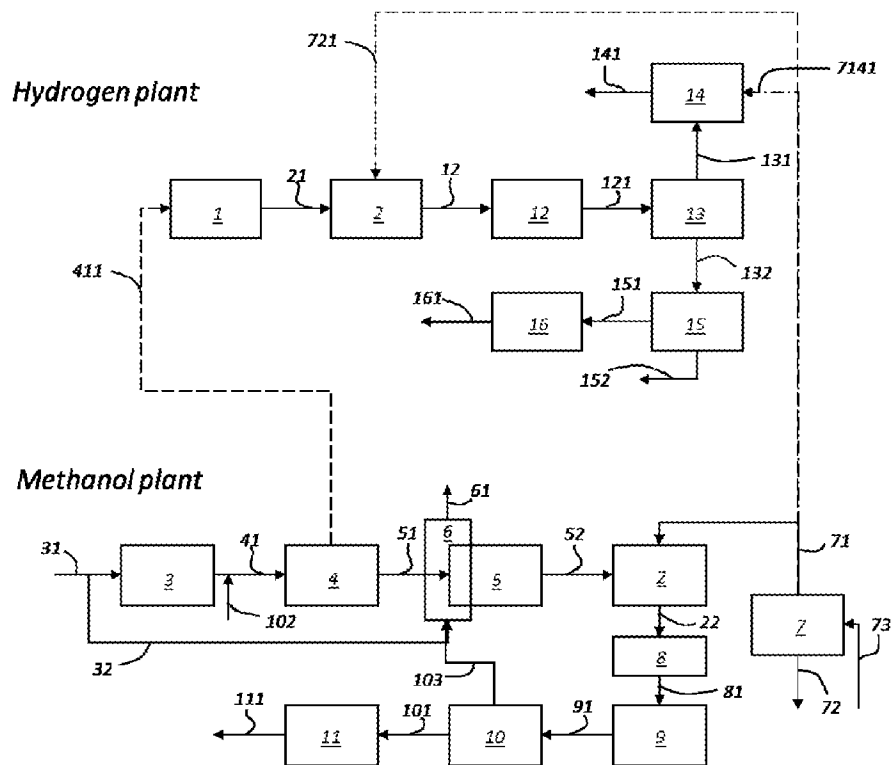


Figure 4



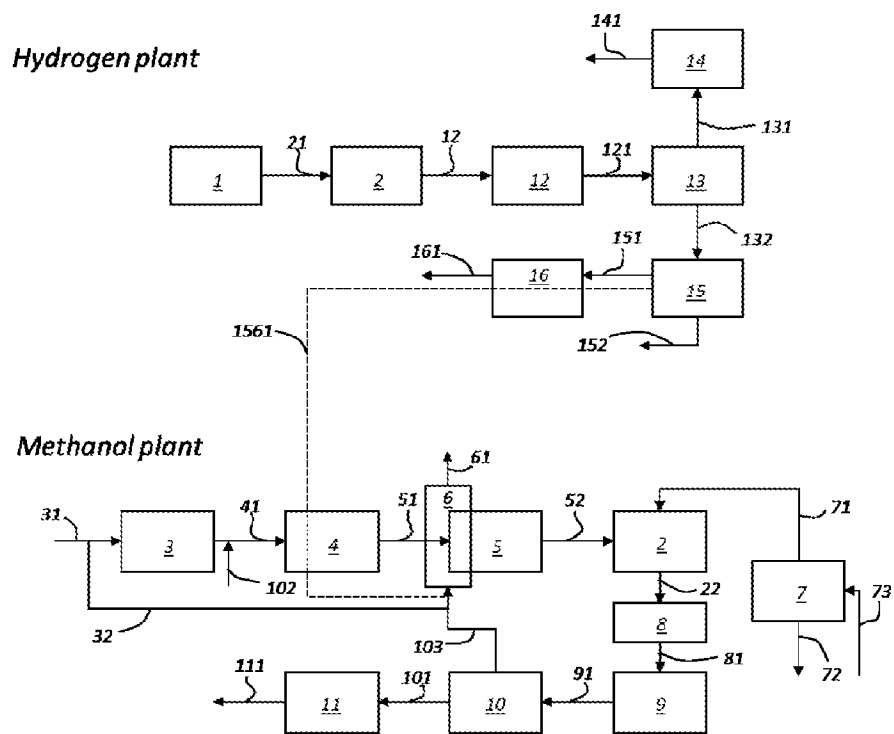


Figure 5

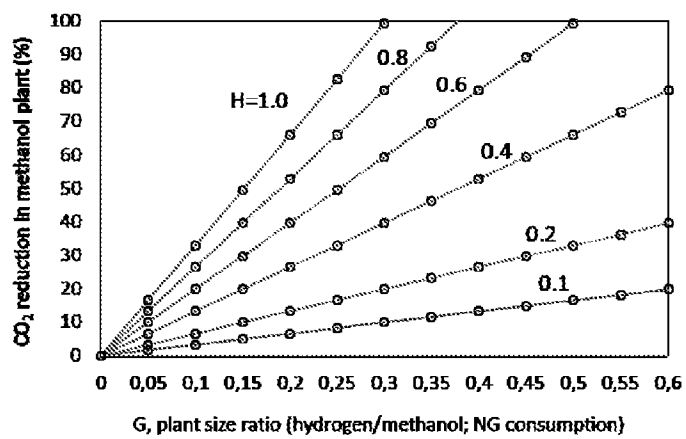


Figure 6

## **GAS PROCESSING**

### **Field**

- 5 The present disclosure relates to the production of hydrogen and carbon dioxide from natural gas. More particularly, embodiments generate hydrogen by performing a gas-heated reforming process and an autothermal reforming process, with heat generated by the autothermal reforming process supplied to the gas-heated reforming process. Advantageously, the production of hydrogen is more efficient than known techniques. The hydrogen production process can also be integrated  
10 into other processes, such as methanol synthesis processes.

### **Background**

- The greenhouse effect and the climate on earth are generally believed to be closely connected to  
15 human made emissions of carbon dioxide, CO<sub>2</sub>. These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines in vehicles. A desirable goal is to reduce the emission of CO<sub>2</sub> to the atmosphere. It is known art to reduce the emission of CO<sub>2</sub> from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen and carbon  
20 dioxide. These components are then separated, where after hydrogen is used for energy generation, heat or in different types of transportation, and carbon dioxide is deposited after compression to desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.
- 25 Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen made by splitting water through electrolysis and compressing hydrogen to typically 700 bar. Liquid hydrogen is being considered for heavier transport like ships and trains. A problem with electrolysis is that it  
30 is expensive and also requires a substantial supply of electrical power. Electrolysis has been calculated as being at least twice as expensive as producing hydrogen by reforming natural gas. These calculations include separation and liquefaction of coproduced CO<sub>2</sub> and payment of tariffs for deposition of CO<sub>2</sub> in underground reservoirs. Another issue with water electrolysis is the calculation of its contribution to the greenhouse gas effect as required electricity may have been  
35 produced from hydrocarbons with significant emission of CO<sub>2</sub> to the atmosphere. Producing hydrogen from natural gas with CO<sub>2</sub> storage is therefore significantly advantageous over hydrogen production by electrolysis.

There are a number of factors that have prevented or postponed production of hydrogen for the transport sector from natural gas. One is that the location of the hydrogen production site should be at an appropriate distance from CO<sub>2</sub> storage facilities. Due to cost of scale, CO<sub>2</sub> storage in off-shore underground reservoirs will have to be supplied by CO<sub>2</sub> from a number of CO<sub>2</sub> emitting facilities. There is also the matter of scale of the hydrogen production. As the demand for hydrogen presently is limited, hydrogen production facilities need to be small compared to what is regarded as world scale processing units. For example, a world scale methanol plant produces, say, 5000-10.000 tons/day. Comparing with a more moderately sized plant of 2500 tons/day, this corresponds to a hydrogen production of 400 tons/day. The hydrogen demand for one ferry or small cruise ship typically is in the range 1-5 tons/day of hydrogen, a hydrogen truck (Nikolai One) has reported a consumption of 4.6 kg per 100 km, and a small passenger train (Alstom Cordura) is designed for 94 kg hydrogen in one tank reaching 600 km.

There is a general need to improve known technology for hydrogen production from natural gas.

#### **Statements of invention**

According to a first aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

Preferably, the method further comprises: saturating the received feed gas with water; adding a hydrogen rich stream to the gas; and pre-reforming the gas; wherein the reforming processes are performed on the pre-reformed gas.

Preferably, the method further comprises: performing a water-gas-shift on the gas output from the reforming processes; separating hydrogen from the shifted gas.

Preferably, the method further comprises compressing and, optionally, liquifying the separated hydrogen.

Preferably, the method further comprises separating carbon dioxide from the shifted gas.

Preferably, the method further comprises compressing and, optionally, liquifying the separated carbon dioxide.

- Preferably, the method further comprises removing sulfur from the received feed gas prior to saturating the received feed gas with water.
- Preferably, the feed gas is natural gas.
- 5 Preferably, the feed gas is a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.
- Preferably, the method further comprises using ZnO to remove sulfur from the feed gas.
- 10 Preferably, the method is performed in a hydrogen production plant.
- Preferably, the method is performed in a hydrogen production plant and one or more further processing plants separate from the hydrogen production plant; and one or more of saturating the received feed gas with water, adding a portion of a hydrogen rich stream to the gas and pre-reforming the gas is performed by a further processing plant.
- 15 Preferably, the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
- 20 Preferably, the added hydrogen rich stream is obtained from a synthesis loop in a methanol synthesis plant.
- 25 Preferably, the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.
- Preferably, the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.
- 30 Preferably, the method further comprises providing the autothermal reforming process with: oxygen from an air separation unit; and/or oxygen or oxygen enriched air from a membrane air separation unit.
- 35 Preferably, the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.
- Preferably, the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.

- Preferably, the water-gas-shift is performed in one reactor
- 5 Preferably, hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.
- 10 Preferably, carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.
- 15 Preferably, hydrogen and/or carbon dioxide is liquified using excess cooling capacity from an auxiliary processing plant, optionally the auxiliary processing plant is an air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.
- 20 Preferably, all, or part of, the separated hydrogen is used to adjust the stoichiometric number of a methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.
- Preferably, all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.
- 25 According to a second aspect of the invention, there is provided a hydrogen production plant arranged to perform the method of any preceding claim.
- 30 According to a third aspect of the invention, there is provided a hydrogen production plant and one or more further processing plants arranged to perform the method of the first aspect.
- Preferably, the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

#### List of Figures

35 Figure 1 shows a reforming process according to an embodiment;

Figure 2 shows a configuration of a methanol synthesis plant;

Figure 3 shows a configuration of a hydrogen production plant according to an embodiment;

Figure 4 shows a configuration of an integrated methanol and hydrogen plants according to an embodiment;

5 Figure 5 shows a configuration of an integrated methanol and hydrogen plants according to an embodiment; and

Figure 6 is a graph that shows the effect of the relative sizes of the methanol and hydrogen plants in integrated methanol and hydrogen plants according to embodiments.

## 10 Description of Embodiments

Embodiments provide a new method for producing hydrogen. Embodiments further include the integration of the method for producing hydrogen according to embodiments into other processes, in particular methanol synthesis processes. Advantageously, the integrated processes provide  
15 improved performance over individual processes.

Syngas is gas containing mainly  $H_2$  and  $CO$ , with some  $CO_2$  and unconverted  $CH_4$ , possibly some higher hydrocarbons and inert gases, and  $H_2O$ . Production and perspectives on syngas production has been described by J. R. Rostrup-Nielsen in *Catalysis Today*, volume 18, pages 305-324, 1993, and in volume 71, pages 243-247, 2002. There are several types of reformers for production of  
20 synthesis gas comprising steam reforming, autothermal reforming and partial oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to  
25 provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.

In a preferred embodiment, cleaning and pre-treatment of natural gas is performed so that the gas  
30 feed mainly comprises methane after these processes. Such cleaning may comprise sulfur removal, e.g. in a  $ZnO$  absorber. Pre-treatment may comprise pre-reforming whereby higher hydrocarbons, such as ethane, are converted by steam to methane and  $CO_2$ . The reforming takes place at a pressure within the interval 10 to 200 bar. It is preferred to use a shift reactor when carrying out embodiments. Steam can be supplied to the shift reactor, but it can also be operated  
35 without supply of steam. At the outlet of the shift reactor a content on carbon basis of  $CO$  up to 2 % by volume, preferably 5% by volume, and methane with 2% by volume, preferably 5% by volume, is preferred.

The following chemical reactions take place by production of synthesis gas and hydrogen by reforming of natural gas:



The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by combination with the partial oxidation in an autothermal reformer. In a steam reformer (SR) natural gas (methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer comprises many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer lies in the temperature area of 950 °C. The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the product stream is from 2.7 to 3.0. A typical synthesis gas produced from a steam reformer contains approximately 3% by volume of methane.

Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR natural gas (methane) is fed together with oxygen or air into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions are driven to equilibrium over a catalyst bed before the synthesis gas is leaving the reactor at approximately 1000-1050 °C. The size of such a unit could be a height of 10-15 meters and a diameter of 5-6 meters. Typical ratio of steam:carbon is from 0.6 to 1.4. The ratio between hydrogen and carbon monoxide in the exit gas is lower than 2. Typical methane slip, i.e. amount of unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR. A further option for reforming natural gas is a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed. The exit temperature for a POX is somewhat higher than for a typical ATR. Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR

and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. SR is in CR operated at milder conditions, i.e. lower outlet temperature, which leads to a high methane slip. The residual methane is reacted in the ATR. The ratio steam:carbon is in the area 1.8-2.4, with a ratio between hydrogen and carbon monoxide in the product gas higher than 2.

From the above, it is clear that the reformer unit has a very large footprint (SR), and that the exit gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB) that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting.

Figure 1 shows a more efficient reforming process according to an embodiment in which the hot exit gas is used to reform part of the natural gas before it enters the autothermal reformer.

It is only known for a combination of ATR with oxygen and a gas-heated-reformer (GHR) to be used in this way for production of methanol. However, the present inventor has found that the same GHR and ATR combination can be used in a hydrogen production process. The hydrogen production process comprises the separation of hydrogen and carbon dioxide after the reforming processes.

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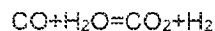
According to embodiments, instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR, then the ATR 2 by stream 21 and finally the heating side of the GHR to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only moderate further cooling before WGS.

25

After reforming of the natural gas and cooling, the gas mixture according to embodiments is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and some CH<sub>4</sub>. Between these components there is an equilibrium relation given by the stoichiometric equation:

30





This reaction is called the water-gas-shift reaction (WGS), and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors are used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. Catalyst in the first step is normally based on chromium/iron, whereas the catalyst in the second step normally is a copper/zinc catalyst. In the shift unit CO and H<sub>2</sub>O are reacted to CO<sub>2</sub> and H<sub>2</sub>, and in known techniques it is often a requirement that the mentioned reaction to a highest possible degree is driven to the right, so that as little CO as possible is present in the gas mixture out of the shift unit. A low content of CO in the mentioned gas mixture again gives a high purity of the H<sub>2</sub>-rich gas stream out of the separation unit. In known art the ratio H<sub>2</sub>O:CO to the shift reactor is high, e.g. equal to 10:1, which gives a high conversion of CO. However, there are other process configurations where different arrangements of WGS are preferred. One such configuration is when hydrogen is separated by a palladium membrane. A Pd membrane requires a certain elevated temperature to operate efficiently. Therefore, only high-temperature WGS may be applied before the membrane. It is also possible to use low-temperature WGS after the membrane and partly recycle the shifted gas.

Gases in the mixture after the shift reactor or the shift reactors can be separated more or less completely based on the different properties of the gas molecules. The most common principles are absorption, adsorption, membranes and cryogenic distillation. CO<sub>2</sub> is an acid gas, and the most widely used method to separate the mentioned gas from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by altering the composition of the liquid or by altering pressure and temperature. For separation of CO<sub>2</sub>, aqueous solutions of alcoholamines can be used. The absorption is taking place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried

out at a relatively high temperature and low pressure. To liberate CO<sub>2</sub> from the amine phase in the stripping unit, stripping steam is usually used. If the partial pressure of CO<sub>2</sub> in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO<sub>2</sub> can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar. Other absorption technologies rely on alternative liquid absorbents like methanol at reduced temperature.

By the use of one or more semipermeable or dense membrane unit, like using a Pd-film, it is possible to achieve that molecules of different size and different properties permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture in question membranes can be selected where H<sub>2</sub> permeates rapidly, whereas CO<sub>2</sub> permeates slowly or not at all, where after separation of the different gas components is achieved. The driving force over the membrane is difference in partial pressure, e.g. of hydrogen between the process gas and the permeate side of a Pd-membrane. As hydrogen in many cases is required at an elevated pressure, one preferred way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. By combining solid membranes and liquid membranes it is also possible to achieve a rapid permeation of CO<sub>2</sub>, while H<sub>2</sub> is kept back.

Another frequently used method in gas separation is pressure-swing adsorption (PSA). PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It is normally operated at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed molecules. In the present mixture of gases, CO, CO<sub>2</sub> and CH<sub>4</sub> are adsorbed, letting the hydrogen pass through at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit.

Embodiments include using any known technique for hydrogen and carbon dioxide separation.

In embodiments of the present invention it is desirable to deposit out-separated CO<sub>2</sub>. Large amounts of CO<sub>2</sub> can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water geological reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO<sub>2</sub> gas has to be brought

to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO<sub>2</sub> gas can be separated from the H<sub>2</sub>/CO<sub>2</sub> mixture at an elevated pressure, significant compression work can be avoided. However, it might be necessary to select between hydrogen and CO<sub>2</sub> to be collected at the high (process) pressure. Hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen will be needed for storage and in transportation applications. As it is more demanding to pressurize hydrogen than CO<sub>2</sub>, separation technologies that provide hydrogen at high pressure is sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen permeable membrane.

Methanol is a commodity used for number of purposes, mainly as a feedstock for production of chemicals. These chemicals comprise formaldehyde, acetic acid and dimethyl ether. Another use is in the petrochemical industry for making olefins through the methanol-to-olefins route, or more selectively by methanol-to-propylene. Methanol is also used as a fuel or a fuel additive. Two widely different applications are in production of the gasoline additive MTBE (methyl-tertbutyl ether) and in manufacture of biodiesel through transesterification of triglycerides. Occasionally, methanol is used directly as a blending component in gasoline or diesel.

Methanol is for the large part produced from natural gas by first making syngas according to eqs. 1-3. Then methanol is produced over a copper based catalyst by the overall reaction



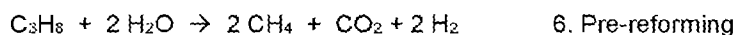
The mechanism is, however thought to be through CO<sub>2</sub>;



CO<sub>2</sub> is partially formed in-situ in the reactor by the water-gas shift reaction



but can also be provided externally. Often the feed contains a certain amount of CO<sub>2</sub> that has been formed by pre-reforming natural gas containing some higher alkanes, e.g. propane;



It follows that the gas consumption in methanol synthesis is dictated by the stoichiometric number (SN):

SN = (P<sub>H<sub>2</sub></sub> - P<sub>CO<sub>2</sub></sub>)/(P<sub>CO</sub> + P<sub>CO<sub>2</sub></sub>) = 2

where P signifies partial pressure.

Figure 2 illustrates one typical configuration of a methanol synthesis plant. The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen rich stream 103 is added to the pretreated natural gas 41 and fed to the pre-reformer 4, ref. eq. 6. The pre-reformed gas 51 is fed to steam reformer 5 that encompasses a combustion chamber 6 to provide heat for the reaction in eq. 2, giving an exhausted gas 61 where carbon in the combined feed (32+103) has been combusted to CO<sub>2</sub>. After partial conversion of methane, the gas 52 is fed to an autothermal reformer 2 for further conversion to the syngas 22 according to eqs. 1 and 3. Oxygen 71 from an air separation unit (7; ASU) is added to the ATR 2. The ASU separates cryogenically air 73 to oxygen and nitrogen 72, sometimes also producing noble gases like argon. Other means for air separation or producing oxygen enriched air are possible, typically using membranes. A steam reformer and an autothermal reformer in series is often called combined reforming (CR). The produced syngas (22) is cooled in a WHB 8 and in subsequent heat exchangers before the gas 81 is entering the methanol synthesis block 9. This synthesis block can contain one or several methanol synthesis reactors and means for gas mixing and recycle of syngas that is not converted to methanol. To suppress production of unwanted byproducts, the composition of the gas fed to the methanol reactor contains surplus hydrogen. The following separation block 10, which is supplied by 91, contains distillation units for separation of methanol and water. Unconverted syngas is partly used as fuel 103 for the SR and partly added before the pre-reformer 4 (102). Finally, methanol, from path 101, is stored 11 before being shipped 111 to customers.

The production of methanol and production of hydrogen have similarities in that both processes rely on reforming natural gas to a syngas mixture comprising major amounts of hydrogen and CO, with some CO<sub>2</sub> and residual methane and water. The present inventor has surprisingly found that these similarities call for novel ways of integration between such process units.

Examples of embodiments are provided below.

#### EMBODIMENT EXAMPLE 1

Production of hydrogen and CO<sub>2</sub> by GHR and ATR according to an embodiment of the present invention.

Figure 3 shows production of hydrogen and CO<sub>2</sub> by combination of ATR 2 and GHR 1 according to an embodiment.

Natural gas, NG, is fed in at 31. NG pretreatment 3 and pre-reforming 4 are performed as described in Figure 2 with units with corresponding reference signs.

5 The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen is added to the ATR by an ASU 7, as described in Figure 2 with units with corresponding reference signs.

10 The produced syngas 12 is shifted to increase the content of hydrogen and CO<sub>2</sub> in the shift reactor or shift reactors 12 to give the shifted gas 121. This gas is subsequently cooled to knock out the water content. Separation process 13 separates CO<sub>2</sub> 131 from the shifted gas, and the CO<sub>2</sub> is compressed 14 and optionally liquified. The produced CO<sub>2</sub> 141 is stored at site and shipped for permanent storage. Hydrogen 151 is separated in the process 15, e.g. by PSA, that separates the gas depleted for CO<sub>2</sub> 132. The rest gas 152 contains remains of CO and CH<sub>4</sub> together with  
15 unseparated CO<sub>2</sub> and hydrogen. The energy in this gas is utilized for fuel in fired heater(s) for preheating of feed gases, or it can be recycled 153 to the ATR 2 for maximum carbon efficiency. Finally, the produced hydrogen is compressed and optionally liquified 16 before being transported to customers.

20 Process simulations of the flow-sheet in Figure 3 using the program HYSYS is based on natural gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher hydrocarbons, 1.5% CO<sub>2</sub> and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. Hydrogen specification is > 99.97 mol% for fuel cells, and specification for CO<sub>2</sub> is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C. The simulations show that production  
25 of 100 kNm<sup>3</sup>/hr hydrogen requires 35.7 kNm<sup>3</sup>/hr of NG and 16.7 kNm<sup>3</sup>/hr of oxygen. 622 tons of CO<sub>2</sub> is captured each year, assuming that the PSA off-gas (152) is used for combustion and the exhaust gas CO<sub>2</sub> emitted to the atmosphere. This gives a CO<sub>2</sub> capture efficiency of 95.4%. Electric power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

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## EMBODIMENT EXAMPLE 2

The use of both an ATR 2 and a GHR 1 in order to produce hydrogen and described in embodiment example 1 is compared with known techniques for producing hydrogen in Table 1.

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| Reformer | NG feed<br>(kNm <sup>3</sup> /hr) | Oxygen feed<br>(kNm <sup>3</sup> /hr) | Captured CO <sub>2</sub><br>(tons/yr) | Capture efficiency<br>(%) | Energy efficiency<br>(%) | Import power<br>(MW) |
|----------|-----------------------------------|---------------------------------------|---------------------------------------|---------------------------|--------------------------|----------------------|
|----------|-----------------------------------|---------------------------------------|---------------------------------------|---------------------------|--------------------------|----------------------|

|                  |      |       |     |      |      |      |
|------------------|------|-------|-----|------|------|------|
| <b>GHR + ATR</b> | 35.7 | 16.7  | 622 | 95.4 | 80.4 | 18.5 |
| <b>ATR</b>       | 38.4 | 23.0  | 681 | 96.4 | 74.5 | 14.6 |
| <b>SR</b>        | 42.0 | (air) | 682 | 95.0 | 74.0 | n.a. |

n.a.: not available

**Table 1**

5 HYSYS simulations for production of 100 kNm<sup>3</sup>/hr hydrogen are provided in Table 1 for the techniques of embodiment example 1 as well as with known techniques.

The GHR 1 and ATR 2 combination according to an embodiment gives significantly lower consumption of natural gas, less CO<sub>2</sub> needs to be captured (capture efficiencies being approximately equal), and the energy efficiency is significantly improved. Compared to using only  
10 an ATR reformer, the GHR 1 and ATR 2 combination requires significantly less imported oxygen. SR has the highest NG consumption and will cost significantly more. The cost drivers in SR are the large reformers, the operation at a lower pressure, and most importantly, very cost demanding capture of CO<sub>2</sub> from flue gas.

### 15 EMBODIMENT EXAMPLE 3

According to a particularly preferred embodiment, the production of hydrogen is integrated with the production of methanol.

20 Process integration between a methanol plant and a hydrogen plant, that is preferably smaller than the methanol plant, is shown in Figure 4. The dashed lines illustrate that, if spare capacity is available or decision to reduce methanol production capacity has been made, that pre-treated NG 411 can be imported to the hydrogen plant. The figure shows import from the pre-reformer 4, but the input can be from any stage from the arrival of NG at the production site. Further, another  
25 dashed line 721 shows that produced oxygen in the ASU of the methanol plant is used in the ATR of the hydrogen plant. Also illustrated, by a dotted dash line 7141, is that extra cooling capacity of the ASU, in the form of oxygen or nitrogen, can be used to cool down the captured CO<sub>2</sub>; alternatively, this capacity can be used to cool down hydrogen.

30 Embodiments include a number of other ways in which the methanol and hydrogen plants can be integrated, such as safety systems, nitrogen blanketing, harbor facilities, maintenance etc.

Advantageously, by integrating a methanol plant and a hydrogen plant, the overall efficiency of both methanol and hydrogen production is improved over the individual efficiencies of separate methanol and hydrogen plants. In addition, the production of methanol is flexible and, by changing the amount of hydrogen production, the amount of methanol production can be increased or  
5 decreased as may be required by both supply and demand fluctuations. Similarly, the production of hydrogen is flexible and, by changing the amount of methanol production, the amount of hydrogen production can be increased or decreased as may be required by both supply and demand fluctuations.

#### 10 EMBODIMENT EXAMPLE 4

According to a particularly preferred embodiment, the production of hydrogen is integrated with the production of methanol. That is to say, the hydrogen generated by the hydrogen plant may also be flexibly provided to the methanol plant.

15 The techniques of embodiment example 4 may be performed either on their own or in addition to those of embodiment example 3.

It is preferable to have an additional sink of hydrogen other than the main purpose of the hydrogen  
20 plant, which would typically be transporting or containing the generated hydrogen for use elsewhere. According to embodiment example 4, an additional possible use of the generated hydrogen is as fuel gas for the combustion chamber 6 in the methanol plant, as shown in Figure 5.

Figure 5 shows a dotted hydrogen supply line 1561 that connects the PSA unit 15 with the  
25 chamber 6. Preferably, compression and/or cooling of the hydrogen in unit 16, is avoided, and/or reduced, and this is a further energy saving.

#### EMBODIMENT EXAMPLE 5

30 According to a particularly preferred embodiment, the techniques of the embodiment example 4 are used to reduce of CO<sub>2</sub> emissions from a methanol plant.

Using the principle of the hydrogen outlet to the method plant as shown in Figure 5, and considering hydrogen production plants of different sizes, it is possible to target a certain reduction  
35 in CO<sub>2</sub> emission in the methanol plant. Most of this emission comes from the burners in the steam reformer and, as an acceptable approximation, it can be assumed that all CO<sub>2</sub> emissions comes from the SR.

A simple relationship between reduction in CO<sub>2</sub> emission from a methanol plant, size of separate hydrogen plant and fraction of hydrogen produced used in the SR burners was found to be:

$$R = k \cdot G \cdot H$$

5

R is percent reduction in overall CO<sub>2</sub> emission during methanol synthesis, G is the NG consumption in the hydrogen plant relative to the methanol plant, H is the fraction of produced hydrogen directed to the SR burners, and k is a parameter specific to the methanol plant at hand. For a given methanol plant employing combined reforming, the parameter k was found to be 330.

10 Calculations using this value of k are shown in Figure 6.

Figure 6 shows effect of the relative sizes of the methanol and hydrogen plants. For example, to reach a CO<sub>2</sub> reduction of 33% the product G\*H must be 0.1. If all produced hydrogen is directed to the methanol plant, this target is achieved with a hydrogen plant using 10% of the NG used to  
15 produce methanol. If 80% of the hydrogen is exported and only 20% used in the SR, the hydrogen plant size in terms of natural gas consumption must be half of the petrochemical plant to achieve the same goal.

It follows that the product G\*H, in the design and operation of a hydrogen plant integrated with a  
20 methanol plant according to embodiments, can be chosen to advantageously reduce greenhouse gas emissions from a methanol plant.

Embodiments include a number of modifications and variations to the above described techniques.

25 For example, embodiments are not restricted to a hydrogen production plant being integrated with a methanol plant and the hydrogen plant may alternatively be integrated with other types of plant, such as one or more of a nitrogen production plant, Fischer-Tropsch synthesis plant, an oil refinery, an air-separation plant or petrochemical plant.

30 The size of the gas-heated reformer in terms of natural gas usage may be 0.5-30% of a typical world scale methanol plant, alternatively 1-20%, further alternatively 1.5-15%.

The product G\*H may be at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2.

35

The hydrogen may be separated before carbon dioxide is separated or the hydrogen may be separated after carbon dioxide is separated.

The separated carbon dioxide may be deposited in a geological reservoir.



The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather, the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with  
5 specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without departing from the spirit and scope of the invention as set forth in the appended claims.

**Claims:**

1. A method of producing hydrogen, the method comprising:
  - 5 receiving a feed gas comprising hydrocarbons; and  
  
performing reforming processes so as to generate hydrogen in dependence on the feed gas;
  - 10 wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and  
  
heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.
  - 15
2. The method according to claim 1, further comprising:
  - satürating the received feed gas with water;
  - 20 adding a hydrogen rich stream to the gas; and  
  
pre-reforming the gas;
  - wherein the reforming processes are performed on the pre-reformed gas.
  - 25
3. The method according to claims 1 or 2, further comprising:
  - performing a water-gas-shift on the gas output from the reforming processes; and
  - 30 separating hydrogen from the shifted gas.
4. The method according to claim 3, further comprising compressing and, optionally, liquifying the separated hydrogen.
- 35 5. The method according to claim 3 or 4, further comprising separating carbon dioxide from the shifted gas.

6. The method according to claim 5, further comprising compressing and, optionally, liquifying the separated carbon dioxide.
- 5 7. The method according to any of claims 2 to 6, further comprising removing sulfur from the received feed gas prior to saturating the received feed gas with water.
8. The method according to any preceding claim, wherein the feed gas is natural gas.
- 10 9. The method according to any of claims 1 to 7, wherein the feed gas is a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.
10. The method according to claim 7 or any claim dependent thereon, further comprising using ZnO to remove sulfur from the feed gas.
- 15 11. The method according to any preceding claim, wherein the method is performed in a hydrogen production plant.
12. The method according to any of claims 2 to 10, wherein the method is performed in a hydrogen production plant and one or more further processing plants separate from the hydrogen production plant; and
- 20 one or more of saturating the received feed gas with water, adding a portion of a hydrogen rich stream to the gas and pre-reforming the gas is performed by a further processing plant.
- 25 13. The method according to claim 12, wherein the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
- 30 14. The method according to claim 13, wherein the added hydrogen rich stream is obtained from a synthesis loop in a methanol synthesis plant.
- 35 15. The method according to any preceding claim, wherein the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.

16. The method according to any preceding claim, wherein the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.
- 5 17. The method according to any preceding claim, further comprising providing the autothermal reforming process with:
- oxygen from an air separation unit; and/or
- 10 oxygen or oxygen enriched air from a membrane air separation unit.
18. The method according to claim 12 or any claim dependent thereon, wherein the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.
- 15 19. The method according to claim 3 or any claim dependent thereon, wherein the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.
- 20 20. The method according to any of claims 3 to 18, wherein the water-gas-shift is performed in one reactor
21. The method according to claim 3 or any claim dependent thereon, wherein hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.
- 25 22. The method according to claim 5 or any claim dependent thereon, wherein carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.
- 30 23. The method according to claim 5 when dependent on claim 3, or any claim dependent on claim 5, wherein hydrogen and/or carbon dioxide is liquified using excess cooling capacity from an auxiliary processing plant, optionally the auxiliary processing plant is an air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.
- 35 24. The method according to claim 3 or any claim dependent thereon, wherein all, or part of, the separated hydrogen is used to adjust the stoichiometric number of a methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.

25. The method according to claim 3 or any claim dependent thereon, wherein all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.
- 5
26. The method according to claim 13 or any claim dependent thereon, wherein the hydrogen production plant is integrated with a methanol synthesis plant; and
- the product  $G \cdot H$  is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2;
- 10
- wherein:
- G is the natural gas consumption in the hydrogen plant relative to the methanol plant; and
- 15
- H is the fraction of hydrogen produced by the hydrogen production plant that is directed to the methanol synthesis plant for consumption in burners therein.
27. A hydrogen production plant arranged to perform the method of any preceding claim.
- 20
28. A hydrogen production plant and one or more further processing plants arranged to perform the method of claim 12 or any claim dependent thereon.
29. A hydrogen production plant and one or more further processing plants according to claim 28, wherein the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
- 25



Application No: GB1802716.9

Examiner: Nicholas Mole

Claims searched: 1-26

Date of search: 27 March 2018

## Patents Act 1977: Search Report under Section 17

### Documents considered to be relevant:

| Category | Relevant to claims                                  | Identity of document and passage or figure of particular relevance                                                                                                                                                                                                                                    |
|----------|-----------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| X,Y      | 1, 3-12, 15-16, 19, 22, 24-25, 27-29 (X) 13, 21 (Y) | WO 2011/077107 A<br>(JOHNSON MATTHEY) see figure 1                                                                                                                                                                                                                                                    |
| X,Y      | 1, 3-12, 17, 18, 21-22, 24, 27-29 (X) 13 (Y)        | US 2016/0264411 A<br>(FILIPPI) see figure 1                                                                                                                                                                                                                                                           |
| X,Y      | 1, 3-9, 11-12, 15-17, 19, 25 (X) 13, 21 (Y)         | G. Manzolini et al. Integration of SEWGS for carbon capture in natural gas combined cycle. Part A: Thermodynamic performances International Journal of Greenhouse Gas Control 5, 200-213, 2011                                                                                                        |
| X,Y      | 1, 3-9, 11-12, 15-17, 19, 25 (X) 13, 21 (Y)         | G. Manzolini et al. Integration of SEWGS for carbon capture in Natural Gas Combined Cycle. Part B: Reference case comparison International Journal of Greenhouse Gas Control 5, 214-225, 2011                                                                                                         |
| X,Y      | 1, 3-8, 12, 15, 19, 25 (X) 13, 21 (Y)               | A, Thallam Thattai et al. System design and exergetic evaluation of a flexible integrated reforming combined cycle (IRCC) power plant system with carbon dioxide (CO <sub>2</sub> ) capture and metal hydride based hydrogen storage International Journal of Greenhouse Gas Control 52, 96-109, 2016 |
| Y        | 13                                                  | WO 2009/155554 A<br>(GTLPETROL) see figure 1 and page 8 lines 3-24                                                                                                                                                                                                                                    |
| Y        | 21                                                  | WO 2013/119465 A<br>(MEMBRANE TECHNOLOGY) see paragraph 52                                                                                                                                                                                                                                            |
| Y        | 21                                                  | WO 2011/150253 A<br>(GTLPETROL) see page 19 line 1 to page 20 line 4                                                                                                                                                                                                                                  |

### Categories:

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| <b>Application Data Sheet 37 CFR 1.76</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                            | Attorney Docket Number | 2110-0010 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                            | Application Number     |           |
| Title of Invention                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |                        |           |
| <p>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.</p> <p>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.</p> |                                            |                        |           |

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| <b>Application Data Sheet 37 CFR 1.76</b> |                                            | Attorney Docket Number | 2110-0010 |
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| <b>Application Data Sheet 37 CFR 1.76</b> |                                            | Attorney Docket Number | 2110-0010 |
|                                           |                                            | Application Number     |           |
| Title of Invention                        | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |                        |           |

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| Attorney Docket Number                  | 2110-0010                                  | Small Entity Status Claimed               | <input type="checkbox"/> |
| Application Type                        | Nonprovisional                             |                                           |                          |
| Subject Matter                          | Utility                                    |                                           |                          |
| Total Number of Drawing Sheets (if any) | 16                                         | Suggested Figure for Publication (if any) |                          |

|                                           |                                            |                        |           |
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| <b>Application Data Sheet 37 CFR 1.76</b> |                                            | Attorney Docket Number | 2110-0010 |
|                                           |                                            | Application Number     |           |
| Title of Invention                        | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |                        |           |

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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).

|                                                        |                          |                                            |
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| 2010174.7                                                                                              | GB                   | 2020-07-02               |                                          |
| Additional Foreign Priority Data may be generated within this form by selecting the <b>Add</b> button. |                      |                          | <a href="#">Add</a>                      |

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

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>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.</p> <p><input type="checkbox"/> 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.</p> |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

|                                           |                                            |           |
|-------------------------------------------|--------------------------------------------|-----------|
| <b>Application Data Sheet 37 CFR 1.76</b> | Attorney Docket Number                     | 2110-0010 |
|                                           | Application Number                         |           |
| Title of Invention                        | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |           |

## 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.

|                                           |                                            |                        |           |
|-------------------------------------------|--------------------------------------------|------------------------|-----------|
| <b>Application Data Sheet 37 CFR 1.76</b> |                                            | Attorney Docket Number | 2110-0010 |
|                                           |                                            | Application Number     |           |
| Title of Invention                        | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |                        |           |

## 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.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                          |                                                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|--------------------------------------------------|
| <b>Applicant</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 1                                        | <a href="#">Remove</a>                           |
| <p>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.</p> <p style="text-align: right;"><a href="#">Clear</a></p> |                                          |                                                  |
| <input checked="" type="radio"/> 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:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                          |                                                  |
| <div style="border: 1px solid black; height: 20px; width: 100%;"></div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                          |                                                  |
| Name of the Deceased or Legally Incapacitated Inventor: <div style="border: 1px solid black; height: 20px; width: 100%;"></div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                          |                                                  |
| If the Applicant is an Organization check here. <input checked="" type="checkbox"/>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                          |                                                  |
| Organization Name                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Reinertsen New Energy AS                 |                                                  |
| <b>Mailing Address Information For Applicant:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                          |                                                  |
| Address 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Leiv Eiriksson Senter                    |                                                  |
| Address 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                          |                                                  |
| City                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Trondheim                                | State/Province                                   |
| Country                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | NO                                       | Postal Code                                      |
| Phone Number                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                          | Fax Number                                       |
| Email Address                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                          |                                                  |
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## 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.

|                                           |                                            |                        |           |
|-------------------------------------------|--------------------------------------------|------------------------|-----------|
| <b>Application Data Sheet 37 CFR 1.76</b> |                                            | Attorney Docket Number | 2110-0010 |
|                                           |                                            | Application Number     |           |
| Title of Invention                        | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |                        |           |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                      |                      |                      |                      |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|----------------------|----------------------|----------------------|
| <b>Assignee</b>   1                                                                                                                                                                                                                                                                                                                                                                                                                                    |                      |                      |                      |                      |
| Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication. |                      |                      |                      |                      |
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| Email Address                                                                                                                                                                                                                                                                                                                                                                                                                                          | <input type="text"/> |                      |                      |                      |
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**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                                                                                                              | /Paul C. Craane/ |           |        | Date (YYYY-MM-DD)   | 2022-09-01 |
| First Name                                                                                                             | Paul             | Last Name | Craane | Registration Number | 38,851     |
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|                                           |                                            | Application Number     |           |
| Title of Invention                        | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |                        |           |

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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(51) International Patent Classification:  
C01B 3/38 (2006.01) C01B 3/48 (2006.01)(21) International Application Number:  
PCT/EP2019/053986(22) International Filing Date:  
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1802716.9 20 February 2018 (20.02.2018) GB(71) Applicant: REINERTSEN NEW ENERGY AS  
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bakken 21, 7030 Trondheim (NO).(74) Agent: J A KEMP, 14 South Square, Gray's Inn, London  
Greater London WC1R 5JJ (GB).(81) Designated States (unless otherwise indicated, for every  
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AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,  
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(54) Title: GAS PROCESSING

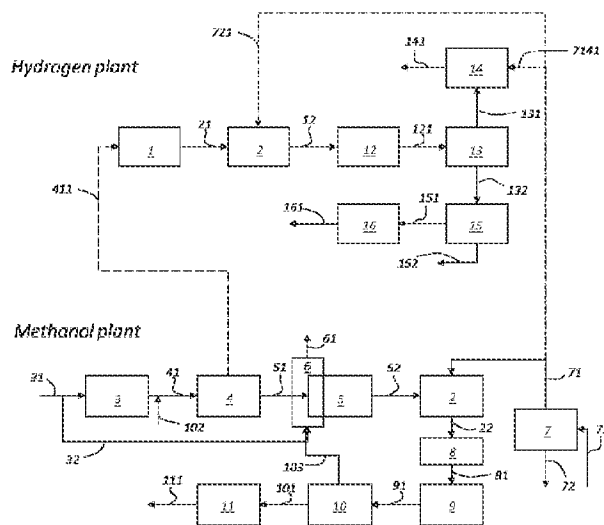


Figure 4

(57) Abstract: Disclosed herein is a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; wherein the method is performed in a hydrogen production plant that is integrated with one or more further processing plants.

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))

## GAS PROCESSING

### Field

- 5 The present disclosure relates to the production of hydrogen. More particularly, embodiments generate hydrogen by performing a gas-heated reforming process and an autothermal reforming process, with heat generated by the autothermal reforming process supplied to the gas-heated reforming process. Advantageously, the production of hydrogen is more efficient than known techniques. The hydrogen production process can also be integrated into other processes, such as methanol synthesis processes.
- 10

### Background

- 15 The greenhouse effect and the climate on earth are generally believed to be closely connected to human made emissions of carbon dioxide, CO<sub>2</sub>. These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines in vehicles. A desirable goal is to reduce the emission of CO<sub>2</sub> to the atmosphere. It is known art to reduce the emission of CO<sub>2</sub> from combustion of natural gas, e.g. by gas reforming and shift technology for preparation of a mixture consisting of hydrogen and carbon
- 20 dioxide. These components are then separated, where after hydrogen is used for energy generation, heat or in different types of transportation, and carbon dioxide is deposited after compression to desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.
- 25 Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen made by splitting water through electrolysis and compressing hydrogen to typically 700 bar. Liquid hydrogen is being considered for heavier transport like ships and trains. A problem with electrolysis is that it
- 30 is expensive and also requires a substantial supply of electrical power. Electrolysis has been calculated as being at least twice as expensive as producing hydrogen by reforming natural gas. These calculations include separation and liquefaction of coproduced CO<sub>2</sub> and payment of tariffs for deposition of CO<sub>2</sub> in underground reservoirs. Another issue with water electrolysis is the calculation of its contribution to the greenhouse gas effect as required electricity may have been
- 35 produced from hydrocarbons with significant emission of CO<sub>2</sub> to the atmosphere. Producing hydrogen from natural gas with CO<sub>2</sub> storage is therefore significantly advantageous over hydrogen production by electrolysis.

There are a number of factors that have prevented or postponed production of hydrogen for the transport sector from natural gas. One is that the location of the hydrogen production site should be at an appropriate distance from CO<sub>2</sub> storage facilities. Due to cost of scale, CO<sub>2</sub> storage in off-shore underground reservoirs will have to be supplied by CO<sub>2</sub> from a number of CO<sub>2</sub> emitting facilities. There is also the matter of scale of the hydrogen production. As the demand for hydrogen presently is limited, hydrogen production facilities need to be small compared to what is regarded as world scale processing units. For example, a world scale methanol plant produces, say, 5000-10.000 metric tons/day. Comparing with a more moderately sized plant of 2500 tons/day, this corresponds to a hydrogen production of 400 metric tons/day. The hydrogen demand for one ferry or small cruise ship typically is in the range 1-5 metric tons/day of hydrogen, a hydrogen truck (Nikolai One) has reported a consumption of 4.6 kg per 100 km, and a small passenger train (Alstom Cordura) is designed for 94 kg hydrogen in one tank reaching 600 km.

There is a general need to improve known technology for hydrogen production from natural gas.

15

#### Statements of invention

According to a first aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; wherein the method is performed in a hydrogen production plant that is integrated with one or more further processing plants.

25

Preferably, the method further comprises: optionally saturating the received feed gas with at least water; and pre-reforming the gas to generate a pre-reformed gas; wherein the reforming processes are performed on the pre-reformed gas.

30 Preferably, the method further comprises adding a hydrogen rich stream to the received feed gas before the feed gas is input to the pre-reforming process.

Preferably, the method further comprises: performing a water-gas-shift on the gas output from the reforming processes; and separating hydrogen from the shifted gas.

35

Preferably, the method further comprises compressing and, optionally, liquifying the separated hydrogen.

- Preferably, the method further comprises separating carbon dioxide from the shifted gas.
- Preferably, the method further comprises compressing and, optionally, liquifying the separated carbon dioxide.
- 5 Preferably, the method further comprises removing sulfur from the received feed gas prior to saturating the received feed gas with water.
- Preferably, ZnO is used to remove sulfur from the feed gas.
- 10 Preferably, the feed gas is natural gas.
- Preferably, the feed gas is a hydrocarbon rich gaseous stream from, or within, an oil refinery and/or a petrochemical plant.
- 15 Preferably, the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
- 20 Preferably, the method is performed in a hydrogen production plant that is integrated with a methanol synthesis plant; and one or both of saturating the received feed gas with water and pre-reforming the gas is performed by the methanol synthesis plant; and the method comprises supplying at least part of the feed gas that is saturated with water, and/or at least part of the pre-reformed gas, from the methanol synthesis plant to the hydrogen plant.
- 25 Preferably, the hydrogen rich stream that is added to the feed gas is generated by a synthesis loop in a methanol synthesis plant.
- Preferably, the method further comprises supplying at least part of any product that is generated in the hydrogen production plant to at least one of the one or more of the further processing plants that the hydrogen production plant is integrated with such that the supplied product can be used by the at least one of the one or more of the further processing plants; and/or supplying at least part of any product that is generated in at least one of the one or more of the further processing plants that the hydrogen production plant is integrated with to the hydrogen production plant such that the supplied product can be used by the hydrogen production plant.
- 30
- 35 Preferably, the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.

Preferably, the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.

5 Preferably, the method further comprises providing the autothermal reforming process with: oxygen from an air separation unit such as a cryogenic air separation unit; oxygen or oxygen enriched air from a membrane air separation unit; and/or oxygen from a pressure or vacuum swing adsorption unit.

10 Preferably, the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.

Preferably, the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.

15

Preferably, the water-gas-shift is performed in a single reactor.

Preferably, hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.

20

Preferably, carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.

25 Preferably, hydrogen and/or carbon dioxide is liquified using the excess cooling capacity of an auxiliary processing plant, wherein optionally the auxiliary processing plant is an air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.

Preferably, the further processing plant is a methanol synthesis plant and all, or part of, the separated hydrogen is used to adjust the stoichiometric number of the methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.

30

Preferably, in use, all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.

35

Preferably, the process of separating hydrogen from the shifted gas comprises generating a rest gas; and the method further comprises using at least part of the rest gas.

Preferably, at least part of the rest gas is used as a fuel for one or more of: pre-heating one or more of the feed gas, the gas input to a pre-treatment process, the gas input to a pre-reforming process and the gas input to the gas-heated reforming process; generating steam for use in a pre-reforming process and/or for adding to the gas stream input to a water gas shift reactor; and powering a gas turbine.

Preferably, at least part of the rest gas is fed into the autothermal reforming process and/or the gas-heated reforming process.

Preferably, the hydrogen production plant is integrated with a methanol synthesis plant; and the product  $G \cdot H$  is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2; wherein:  $G$  is the natural gas consumption in the hydrogen plant relative to the methanol plant; and  $H$  is the fraction of hydrogen produced by the hydrogen production plant that is directed to the methanol synthesis plant for consumption in burners therein.

According to a second aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; the method further comprising saturating the received feed gas with water; and pre-reforming the gas to generate pre-reformed gas; wherein the reforming processes are performed on the pre-reformed gas.

According to a third aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; the method further comprising: performing a water-gas-shift on the gas output from the reforming processes; and separating hydrogen from the shifted gas; wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and the method further comprises using at least part of the rest gas.

According to a fourth aspect of the invention, there is provided a hydrogen production plant arranged to perform the method of the second aspect or the third aspect.



According to a fifth aspect of the invention, there is provided a hydrogen production plant and one or more further processing plants arranged to perform the method of the first aspect.

Preferably, the one or more further processing plants include any of a methanol synthesis plant, a  
5 nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

### List of Figures

10 Figure 1 shows a reforming process according to an embodiment;

Figure 2 shows a configuration of a methanol synthesis plant;

15 Figure 3 shows a configuration of a hydrogen production plant according to an embodiment;

Figure 4 shows a configuration of an integrated methanol and hydrogen plants according to an embodiment;

20 Figure 5 shows a configuration of an integrated methanol and hydrogen plants according to an embodiment; and

Figure 6 is a graph that shows the effect of the relative sizes of the methanol and hydrogen plants in integrated methanol and hydrogen plants according to embodiments.

### 25 Description of Embodiments

Embodiments provide a new method for producing hydrogen. Embodiments further include the integration of the method for producing hydrogen according to embodiments into other processes, in particular methanol synthesis processes. Advantageously, the integrated processes provide  
30 improved performance over individual processes.

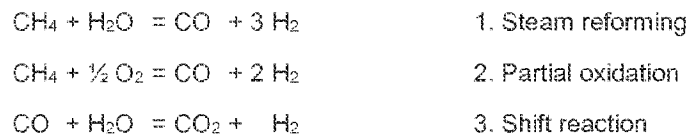
Syngas is gas containing mainly  $H_2$  and  $CO$ , with some  $CO_2$  and unconverted  $CH_4$ , possibly some higher hydrocarbons and inert gases, and  $H_2O$ . Production and perspectives on syngas production has been described by J. R. Rostrup-Nielsen in Catalysis Today, volume 18, pages 305-324, 1993,  
35 and in volume 71, pages 243-247, 2002. There are several types of reformers for production of synthesis gas comprising steam reforming, autothermal reforming and partial oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in

series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.

5

In a preferred embodiment, cleaning and pre-treatment of natural gas is performed so that the gas feed mainly comprises methane after these processes. Such cleaning may comprise sulfur removal, e.g. in a ZnO absorber. Pre-treatment may comprise pre-reforming whereby higher hydrocarbons, such as ethane, are converted by steam to methane and CO<sub>2</sub>. The reforming takes place at a pressure within the interval 10 to 200 bar. It is preferred to use a shift reactor when carrying out embodiments. Steam can be supplied to the shift reactor, but it can also be operated without supply of steam. At the outlet of the shift reactor a content on carbon basis of CO up to 2 % by volume, preferably 5% by volume, and methane with 2% by volume, preferably 5% by volume, is preferred.

15 The following chemical reactions take place by production of synthesis gas and hydrogen by reforming of natural gas:



The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by combination with the partial oxidation in an autothermal reformer. In a steam reformer (SR) natural gas (methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer comprises many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer lies in the temperature area of 950 °C. The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the product stream is from 2.7 to 3.0. A typical synthesis gas produced from a steam reformer contains approximately 3% by volume of methane.

30 Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR natural gas (methane) is fed together with oxygen or air

into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions are driven to equilibrium over a catalyst bed before the  
5 synthesis gas is leaving the reactor at approximately 1000-1050 °C. The size of such a unit could be a height of 10-15 meters and a diameter of 5-6 meters. Typical ratio of steam:carbon is from 0.6 to 1.4. The ratio between hydrogen and carbon monoxide in the exit gas is lower than 2. Typical methane slip, i.e. amount of unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR. A further option for reforming natural gas is a  
10 partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed. The exit temperature for a POX is somewhat higher than for a typical ATR. Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the  
15 efforts on the two reformers. SR is in CR operated at milder conditions, i.e. lower outlet temperature, which leads to a high methane slip. The residual methane is reacted in the ATR. The ratio steam:carbon is in the area 1.8-2.4, with a ratio between hydrogen and carbon monoxide in the product gas higher than 2.

From the above, it is clear that the reformer unit has a very large footprint (SR), and that the exit  
20 gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB) that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting.

Figure 1 shows a more efficient reforming process according to an embodiment in which the hot exit gas is used to reform part of the natural gas before it enters the autothermal reformer.

25 It is only known for a combination of ATR with oxygen and a gas-heated-reformer (GHR) to be used in this way for production of methanol. However, the present inventor has found that the same GHR and ATR combination can be used in a hydrogen production process. The hydrogen production process comprises the separation of hydrogen and carbon dioxide after the reforming processes.

30 According to embodiments, instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR, then the ATR 2 by stream 21 and finally the heating side of the GHR to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only  
35 moderate further cooling before WGS.

After reforming of the natural gas and cooling, the gas mixture according to embodiments is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and some CH<sub>4</sub>. Between these components there is an equilibrium relation given by the stoichiometric equation:

5



This reaction is called the water-gas-shift reaction (WGS), and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors are used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. Catalyst in the first step is normally based on chromium/iron, whereas the catalyst in the second step normally is a copper/zinc catalyst. In the shift unit CO and H<sub>2</sub>O are reacted to CO<sub>2</sub> and H<sub>2</sub>, and in known techniques it is often a requirement that the mentioned reaction to a highest possible degree is driven to the right, so that as little CO as possible is present in the gas mixture out of the shift unit. A low content of CO in the mentioned gas mixture again gives a high purity of the H<sub>2</sub>-rich gas stream out of the separation unit. In known art the ratio H<sub>2</sub>O:CO to the shift reactor is high, e.g. equal to 10:1, which gives a high conversion of CO. However, there are other process configurations where different arrangements of WGS are preferred. One such configuration is when hydrogen is separated by a palladium membrane. A Pd membrane requires a certain elevated temperature to operate efficiently. Therefore, only high-temperature WGS may be applied before the membrane. It is also possible to use low-temperature WGS after the membrane and partly recycle the shifted gas.

Gases in the mixture after the shift reactor or the shift reactors can be separated more or less completely based on the different properties of the gas molecules. The most common principles are absorption, adsorption, membranes and cryogenic distillation. CO<sub>2</sub> is an acid gas, and the most widely used method to separate the mentioned gas from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by

- altering the composition of the liquid or by altering pressure and temperature. For separation of CO<sub>2</sub>, aqueous solutions of alcoholamines can be used. The absorption is taking place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO<sub>2</sub> from the amine phase in the stripping unit, stripping steam is usually used. If the partial pressure of CO<sub>2</sub> in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO<sub>2</sub> can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar. Other absorption technologies rely on alternative liquid absorbents like methanol at reduced temperature.
- 10 By the use of one or more semipermeable or dense membrane unit, like using a Pd-film, it is possible to achieve that molecules of different size and different properties permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture in question membranes can be selected where H<sub>2</sub> permeates rapidly, whereas CO<sub>2</sub> permeates slowly or not at all, where after separation of the different gas components is achieved. The driving force over the membrane is difference in partial pressure, e.g. of hydrogen between the process gas and the permeate side of a Pd-membrane. As hydrogen in many cases is required at an elevated pressure, one preferred way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. By combining solid membranes and liquid membranes it is also possible to achieve a rapid permeation of CO<sub>2</sub>, while H<sub>2</sub> is kept back.
- 15 Another frequently used method in gas separation is pressure-swing adsorption (PSA). PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It is normally operated at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed molecules. In the present mixture of gases, CO, CO<sub>2</sub> and CH<sub>4</sub> are adsorbed, letting the hydrogen pass through at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit.
- 25 Embodiments include using any known technique for hydrogen and carbon dioxide separation.
- In embodiments of the present invention it is desirable to deposit out-separated CO<sub>2</sub>. Large amounts of CO<sub>2</sub> can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water geological reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated commercially. In these storage forms the CO<sub>2</sub> gas has to be brought

to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO<sub>2</sub> gas can be separated from the H<sub>2</sub>/CO<sub>2</sub> mixture at an elevated pressure, significant compression work can be avoided. However, it might be necessary to select between hydrogen and CO<sub>2</sub> to be collected at the high (process) pressure. Hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen will be needed for storage and in transportation applications. As it is more demanding to pressurize hydrogen than CO<sub>2</sub>, separation technologies that provide hydrogen at high pressure is sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen permeable membrane.

Methanol is a commodity used for number of purposes, mainly as a feedstock for production of chemicals. These chemicals comprise formaldehyde, acetic acid and dimethyl ether. Another use is in the petrochemical industry for making olefins through the methanol-to-olefins route, or more selectively by methanol-to-propylene. Methanol is also used as a fuel or a fuel additive. Two widely different applications are in production of the gasoline additive MTBE (methyl-tertbutyl ether) and in manufacture of biodiesel through transesterification of triglycerides. Occasionally, methanol is used directly as a blending component in gasoline or diesel.

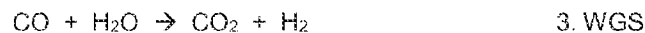
Methanol is for the large part produced from natural gas by first making syngas according to eqs. 1-3. Then methanol is produced over a copper based catalyst by the overall reaction



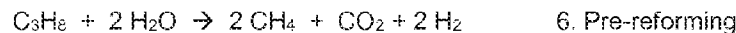
The mechanism is, however thought to be through CO<sub>2</sub>;



CO<sub>2</sub> is partially formed in-situ in the reactor by the water-gas shift reaction



but can also be provided externally. Often the feed contains a certain amount of CO<sub>2</sub> that has been formed by pre-reforming natural gas containing some higher alkanes, e.g. propane;



It follows that the gas consumption in methanol synthesis is dictated by the stoichiometric number (SN):

$$\text{SN} = (\text{P}_{\text{H}_2} - \text{P}_{\text{CO}_2})/(\text{P}_{\text{CO}} + \text{P}_{\text{CO}_2}) = 2$$

where P signifies partial pressure.

Figure 2 illustrates one typical configuration of a methanol synthesis plant. The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen rich stream 103 is added to the pretreated natural gas 41 and fed to the pre-reformer 4, ref. eq. 6. The pre-reformed gas 51 is fed to steam reformer 5 that encompasses a combustion chamber 6 to provide heat for the reaction in eq. 2, giving an exhausted gas 61 where carbon in the combined feed (32+103) has been combusted to CO<sub>2</sub>. After partial conversion of methane, the gas 52 is fed to an autothermal reformer 2 for further conversion to the syngas 22 according to eqs. 1 and 3. Oxygen 71 from an air separation unit (7; ASU) is added to the ATR 2. The ASU separates cryogenically air 73 to oxygen and nitrogen 72, sometimes also producing noble gases like argon. Other means for air separation or producing oxygen enriched air are possible, typically using membranes. A steam reformer and an autothermal reformer in series is often called combined reforming (CR). The produced syngas (22) is cooled in a WHB 8 and in subsequent heat exchangers before the gas 81 is entering the methanol synthesis block 9. This synthesis block can contain one or several methanol synthesis reactors and means for gas mixing and recycle of syngas that is not converted to methanol. To suppress production of unwanted byproducts, the composition of the gas fed to the methanol reactor contains surplus hydrogen. The following separation block 10, which is supplied by 91, contains distillation units for separation of methanol and water. Unconverted syngas is partly used as fuel 103 for the SR and partly added before the pre-reformer 4 (102). Finally, methanol, from path 101, is stored 11 before being shipped 111 to customers.

The production of methanol and production of hydrogen have similarities in that both processes rely on reforming natural gas to a syngas mixture comprising major amounts of hydrogen and CO, with some CO<sub>2</sub> and residual methane and water. The present inventor has surprisingly found that these similarities call for novel ways of integration between such process units.

Examples of embodiments are provided below.

#### EMBODIMENT EXAMPLE 1

Production of hydrogen and CO<sub>2</sub> by GHR and ATR according to an embodiment of the present invention.

Figure 3 shows production of hydrogen and CO<sub>2</sub> by combination of ATR 2 and GHR 1 according to an embodiment.

Natural gas, NG, is fed in at 31. NG pretreatment 3 and pre-reforming 4 are performed as described in Figure 2 with units with corresponding reference signs.

The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen may be added to the ATR by an ASU 7, as described in Figure 2 with units with  
 5 corresponding reference signs. It should be understood that embodiments include any other means for producing oxygen, or air enriched in oxygen, such as by using vacuum or pressure swing adsorption, or by using a membrane.

The produced syngas 12 is shifted to increase the content of hydrogen and CO<sub>2</sub> in one or more  
 10 shift reactors 12, i.e. water gas shift reactor(s) 12, to produce the shifted gas 121. Steam may be added to the gas mixture before the gas mixture is input into the shift reactor(s) 12. The addition of steam increases the efficiency of the shift reaction. The shifted gas 121 may be subsequently cooled to remove its water content. Separation process 13 separates CO<sub>2</sub> 131 from the shifted gas, and the CO<sub>2</sub> is compressed 14 and optionally liquified. The produced CO<sub>2</sub> 141 may be stored at  
 15 site, shipped for permanent storage or directly injected into a geological formation for storage. Hydrogen 151 is separated in the process 15, e.g. by PSA, that separates the hydrogen from the gas 132 that has already been depleted of CO<sub>2</sub> by the process 13. The separate outputs from the process 15 are hydrogen and a rest gas. The rest gas 152 contains remnants of CO and CH<sub>4</sub> together with unseparated CO<sub>2</sub> and hydrogen. As described in more detail later, the energy in the  
 20 rest gas may be utilized for fuel in fired heater(s) for preheating of feed gases, or it can be recycled 153 to the GHR 1 and/or ATR 2 for maximum carbon efficiency. Finally, the produced hydrogen is compressed and optionally liquified 16 before being transported to customers.

Process simulations of the flow-sheet in Figure 3 using the program HYSYS is based on natural  
 25 gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher hydrocarbons, 1.5% CO<sub>2</sub> and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. Hydrogen specification is > 99.97 mol% for fuel cells, and specification for CO<sub>2</sub> is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C. The simulations show that production of 100 kNm<sup>3</sup>/hr hydrogen requires 35.7 kNm<sup>3</sup>/hr of NG and 16.7 kNm<sup>3</sup>/hr of oxygen. 622 tons of  
 30 CO<sub>2</sub> is captured each year, assuming that the PSA off-gas (152) is used for combustion and the exhaust gas CO<sub>2</sub> emitted to the atmosphere. This gives a CO<sub>2</sub> capture efficiency of 95.4%. Electric power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

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## EMBODIMENT EXAMPLE 2



The use of both an ATR 2 and a GHR 1 in order to produce hydrogen and described in embodiment example 1 is compared with known techniques for producing hydrogen in Table 1.

| Reformer  | NG<br>feed<br>(kNm <sup>3</sup> /hr) | Oxygen<br>feed<br>(kNm <sup>3</sup> /hr) | Captured<br>CO <sub>2</sub><br>(metric<br>tons/yr) | Capture<br>efficiency<br>(%) | Energy<br>efficiency<br>(%) | Import<br>power<br>(MW) |
|-----------|--------------------------------------|------------------------------------------|----------------------------------------------------|------------------------------|-----------------------------|-------------------------|
| GHR + ATR | 35.7                                 | 16.7                                     | 622                                                | 95.4                         | 80.4                        | 18.5                    |
| ATR       | 38.4                                 | 23.0                                     | 681                                                | 96.4                         | 74.5                        | 14.6                    |
| SR        | 42.0                                 | (air)                                    | 682                                                | 95.0                         | 74.0                        | n.a.                    |

n.a.: not available

#### 5 Table 1

HYSYS simulations for production of 100 kNm<sup>3</sup>/hr hydrogen are provided in Table 1 for the techniques of embodiment example 1 as well as with known techniques.

- 10 The GHR 1 and ATR 2 combination according to an embodiment gives significantly lower consumption of natural gas, less CO<sub>2</sub> needs to be captured (capture efficiencies being approximately equal), and the energy efficiency is significantly improved. Compared to using only an ATR reformer, the GHR 1 and ATR 2 combination requires significantly less imported oxygen. SR has the highest NG consumption and will cost significantly more. The cost drivers in SR are the
- 15 large reformers, the operation at a lower pressure, and most importantly, very cost demanding capture of CO<sub>2</sub> from flue gas.

#### EMBODIMENT EXAMPLE 3

- 20 In the present embodiment, both an ATR 2 and a GHR 1 are used to produce hydrogen and CO<sub>2</sub>, as already described in embodiment example 1 with reference to Figure 3. The present embodiment further improves the efficiency of the overall processes by using the rest gas 152 that remains after the hydrogen separation process 15. The rest gas may alternatively be referred to as a tail gas or recycle gas.

25

The rest gas may comprise three components. These are pre-treated natural gas 41 or pre-reformed natural gas 11 that has not been converted to syngas by the GHR and ATR processes;

- CO that has not been shifted in the shift reactor; and CO<sub>2</sub> and hydrogen constituents left after the respective separation processes 13 and 15. The first of these components arise mainly due to equilibrium restrictions in reforming methane to CO and hydrogen. The higher the temperature in the reforming process, the lower the amount of methane is left unconverted. The second
- 5 component of the rest gas is CO that due to equilibrium or kinetic limitations has not been shifted to CO<sub>2</sub>. The last component of the rest gas, gas constituents left after separation, is due to inadequate separation of CO<sub>2</sub> and hydrogen as 100% separation seldom can be achieved; with the possible exception of when dense separation membranes are used.
- 10 The rest gas 152 and/or 153 may therefore comprise any of CH<sub>4</sub>, CO, H<sub>2</sub> and CO<sub>2</sub> as well as possible traces of water and some inert gasses, such as nitrogen. The present embodiment comprises using the energy rich components of the rest gas. For example, the rest gas may be used as a fuel in fired heater(s) for the preheating of the feed gas at one or more of the stages that process the feed gas. The feed gas, that may be natural gas, may be heated at one or more of:
- 15 immediately prior to its input into the pre-treatment 3, immediately prior to its input into the pre-reformer 4 and immediately prior to its input into the GHR 1. The rest gas may also be used as a fuel for generating steam 102 that is added before the pre-reformer and before the WGS reactor 12.
- 20 The rest gas may also be used as a fuel for a separate gas turbine, for example to generate electricity.
- The rest gas 153 may also be recycled by feeding it back to the ATR 2, shown by 153 in Figure 3, and/or to the GHR 1, to improve the carbon utilization efficiency. A purge of inert gasses may be
- 25 applied to the gas stream 153 so that a large amount of inert gasses do not accumulate.

The energy in the rest gas may therefore be used to advantageously increase the efficiency of the processes.

#### 30 EMBODIMENT EXAMPLE 4

According to a particularly preferred embodiment, the production of hydrogen is integrated with the production of methanol.

- 35 Process integration between a methanol plant and a hydrogen plant, that is preferably smaller than the methanol plant, is shown in Figure 4. The dashed lines illustrate that, if spare capacity is available or decision to reduce methanol production capacity has been made, that pre-treated NG 411 can be imported to the hydrogen plant. The figure shows import from the pre-reformer 4, but

- the input can be from any stage from the arrival of NG at the production site. Further, another dashed line 721 shows that produced oxygen in the ASU of the methanol plant is used in the ATR of the hydrogen plant. Also illustrated, by a dotted dash line 7141, is that extra cooling capacity of the ASU, in the form of oxygen or nitrogen, can be used to cool down the captured CO<sub>2</sub>;
- 5 alternatively, this capacity can be used to cool down hydrogen.

Embodiments include a number of other ways in which the methanol and hydrogen plants can be integrated, such as safety systems, nitrogen blanketing, harbor facilities, maintenance etc.

- 10 Advantageously, by integrating a methanol plant and a hydrogen plant, the overall efficiency of both methanol and hydrogen production is improved over the individual efficiencies of separate methanol and hydrogen plants. In addition, the production of methanol is flexible and, by changing the amount of hydrogen production, the amount of methanol production can be increased or decreased as may be required by both supply and demand fluctuations. Similarly, the production
- 15 of hydrogen is flexible and, by changing the amount of methanol production, the amount of hydrogen production can be increased or decreased as may be required by both supply and demand fluctuations.

#### EMBODIMENT EXAMPLE 5

- 20 According to a particularly preferred embodiment, the production of hydrogen is integrated with the production of methanol. That is to say, the hydrogen generated by the hydrogen plant may also be flexibly provided to the methanol plant.
- 25 The techniques of embodiment example 5 may be performed either on their own or in addition to those of embodiment example 4.

- It is preferable to have an additional sink of hydrogen other than the main purpose of the hydrogen plant, which would typically be transporting or containing the generated hydrogen for use
- 30 elsewhere. According to embodiment example 5, an additional possible use of the generated hydrogen is as fuel gas for the combustion chamber 6 in the methanol plant, as shown in Figure 5.

- Figure 5 shows a dotted hydrogen supply line 1561 that connects the PSA unit 15 with the chamber 6. Preferably, compression and/or cooling of the hydrogen in unit 16, is avoided, and/or
- 35 reduced, and this is a further energy saving.

#### EMBODIMENT EXAMPLE 6

According to a particularly preferred embodiment, the techniques of the embodiment example 5 are used to reduce CO<sub>2</sub> emissions from a methanol plant.

Using the principle of the hydrogen outlet to the method plant as shown in Figure 5, and  
 5 considering hydrogen production plants of different sizes, it is possible to target a certain reduction in CO<sub>2</sub> emission in the methanol plant. Most of this emission comes from the burners in the steam reformer and, as an acceptable approximation, it can be assumed that all CO<sub>2</sub> emissions comes from the SR.

10 A simple relationship between reduction in CO<sub>2</sub> emission from a methanol plant, size of separate hydrogen plant and fraction of hydrogen produced used in the SR burners was found to be:

$$R = k \cdot G \cdot H$$

15 R is percent reduction in overall CO<sub>2</sub> emission during methanol synthesis, G is the NG consumption in the hydrogen plant relative to the methanol plant, H is the fraction of produced hydrogen directed to the SR burners, and k is a parameter specific to the methanol plant at hand. For a given methanol plant employing combined reforming, the parameter k was found to be 330. Calculations using this value of k are shown in Figure 6.

20 Figure 6 shows effect of the relative sizes of the methanol and hydrogen plants. For example, to reach a CO<sub>2</sub> reduction of 33% the product G\*H must be 0.1. If all produced hydrogen is directed to the methanol plant, this target is achieved with a hydrogen plant using 10% of the NG used to produce methanol. If 80% of the hydrogen is exported and only 20% used in the SR, the hydrogen  
 25 plant size in terms of natural gas consumption must be half of the petrochemical plant to achieve the same goal.

It follows that the product G\*H, in the design and operation of a hydrogen plant integrated with a methanol plant according to embodiments, can be chosen to advantageously reduce greenhouse  
 30 gas emissions from a methanol plant.

Embodiments include a number of modifications and variations to the above described techniques.

For example, embodiments are not restricted to a hydrogen production plant being integrated with  
 35 a methanol plant and the hydrogen plant may alternatively be integrated with other types of plant, such as one or more of a nitrogen production plant, Fischer-Tropsch synthesis plant, an oil refinery, an air-separation plant or petrochemical plant.

The size of the gas-heated reformer in terms of natural gas usage may be 0.5-30% of a typical world scale methanol plant, alternatively 1-20%, further alternatively 1.5-15%.

5 The product  $G^*H$  may be at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2.

Figure 3 shows hydrogen and carbon dioxide being separated for a gas mixture in the separated process 13 and 15. Embodiments also include the hydrogen being separated from the gas mixture before the carbon dioxide is separated from the gas mixture, or the hydrogen and carbon dioxide  
10 may be separated from the gas mixture at the same time in a single process. The separated carbon dioxide may be used, stored and/or deposited in a geological reservoir.

Embodiments include the following numbered clauses:

- 15 1. A method of producing hydrogen, the method comprising:
- receiving a feed gas comprising hydrocarbons; and
- performing reforming processes so as to generate hydrogen in dependence on the feed  
20 gas;
- wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and
- 25 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.
2. The method according to clause 1, further comprising:
- 30 saturating the received feed gas with water;
- adding a hydrogen rich stream to the gas; and
- pre-reforming the gas;
- 35 wherein the reforming processes are performed on the pre-reformed gas.

3. The method according to clauses 1 or 2, further comprising:
- performing a water-gas-shift on the gas output from the reforming processes; and
- 5 separating hydrogen from the shifted gas.
4. The method according to clause 3, further comprising compressing and, optionally, liquifying the separated hydrogen.
- 10 5. The method according to clause 3 or 4, further comprising separating carbon dioxide from the shifted gas.
6. The method according to clause 5, further comprising compressing and, optionally, liquifying the separated carbon dioxide.
- 15 7. The method according to any of clauses 2 to 6, further comprising removing sulfur from the received feed gas prior to saturating the received feed gas with water.
8. The method according to any preceding clause, wherein the feed gas is natural gas.
- 20 9. The method according to any of clauses 1 to 7, wherein the feed gas is a hydrocarbon rich gaseous stream from or within an oil refinery, or a petrochemical plant.
10. The method according to clause 7 or any clause dependent thereon, further comprising
- 25 using ZnO to remove sulfur from the feed gas.
11. The method according to any preceding clause, wherein the method is performed in a hydrogen production plant.
- 30 12. The method according to any of clauses 2 to 10, wherein the method is performed in a hydrogen production plant and one or more further processing plants separate from the hydrogen production plant; and

one or more of saturating the received feed gas with water, adding a portion of a hydrogen rich stream to the gas and pre-reforming the gas is performed by a further processing plant.

- 5        13. The method according to clause 12, wherein the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.
- 10       14. The method according to clause 13, wherein the added hydrogen rich stream is obtained from a synthesis loop in a methanol synthesis plant.
- 15       15. The method according to any preceding clause, wherein the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.
- 16       16. The method according to any preceding clause, wherein the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.
- 20       17. The method according to any preceding clause, further comprising providing the autothermal reforming process with:
- 25       oxygen from an air separation unit; and/or
- 30       oxygen or oxygen enriched air from a membrane air separation unit.
18. The method according to clause 12 or any clause dependent thereon, wherein the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.
19. The method according to clause 3 or any clause dependent thereon, wherein the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.
- 35       20. The method according to any of clauses 3 to 18, wherein the water-gas-shift is performed in one reactor

21. The method according to clause 3 or any clause dependent thereon, wherein hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.
- 5 22. The method according to clause 5 or any clause dependent thereon, wherein carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.
23. The method according to clause 5 when dependent on clause 3, or any clause dependent on clause 5, wherein hydrogen and/or carbon dioxide is liquified using excess cooling capacity from an auxiliary processing plant, optionally the auxiliary processing plant is an  
10 air-separation plant and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.
24. The method according to clause 3 or any clause dependent thereon, wherein all, or part of,  
15 the separated hydrogen is used to adjust the stoichiometric number of a methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.
25. The method according to clause 3 or any clause dependent thereon, wherein all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an auxiliary  
20 processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.
26. The method according to clause 13 or any clause dependent thereon, wherein the hydrogen production plant is integrated with a methanol synthesis plant; and  
25 the product  $G \cdot H$  is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2;
- wherein:
- 30  $G$  is the natural gas consumption in the hydrogen plant relative to the methanol plant; and
- $H$  is the fraction of hydrogen produced by the hydrogen production plant that is directed to the methanol synthesis plant for consumption in burners therein.
- 35 27. A hydrogen production plant arranged to perform the method of any preceding clause.



28. A hydrogen production plant and one or more further processing plants arranged to perform the method of clause 12 or any clause dependent thereon.

5        29. A hydrogen production plant and one or more further processing plants according to clause 28, wherein the one or more further processing plants include a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.

10       In a particularly preferred embodiment, a hydrogen production plant is integrated with a further process plant, such as a methanol production plant, as described throughout the present document.

15       In another particularly preferred embodiment, a hydrogen production plant comprises a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process; the method further comprising saturating the  
20       received feed gas with water; and pre-reforming the gas to generate pre-reformed gas; wherein the reforming processes are performed on the pre-reformed gas.

25       The hydrogen production plant according to the present embodiment may be a standalone hydrogen production plant or integrated with a further processing plant, such as a methanol production plant, as described throughout the present document. The hydrogen production plant according to the present embodiment, and when included the further processing plant, may include any of the features of a hydrogen production plant and/or further processing plant as set out in the above numbered clauses and/or described throughout the present document.

30       In another particularly preferred embodiment, a hydrogen production plant comprises a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons; and performing reforming processes so as to generate hydrogen in dependence on the feed gas; wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is  
35       supplied to the gas-heated reforming process; the method further comprising: performing a water-gas-shift on the gas output from the reforming processes; and separating hydrogen from the shifted

gas; wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and the method further comprises using at least part of the rest gas.

5 Preferably, at least part of the rest gas is used as a fuel for one or more of: pre-heating one or more of the feed gas, the gas input to a pre-treatment process, the gas input to a pre-reforming process and the gas input to the gas-heated reforming process; generating steam for use in a pre-reforming process and/or for adding to the gas stream input to a water gas shift reactor; and powering a gas turbine.

10 Preferably, at least part of the rest gas is fed into the autothermal reforming process and gas-heated reforming process.

15 The hydrogen production plant according to the present embodiment may be a standalone hydrogen production plant or integrated with a further processing plant, such as a methanol production plant, as described throughout the present document. The hydrogen production plant according to the present embodiment, and when included the further processing plant, may include any of the features of a hydrogen production plant and/or further processing plant as set out in the above numbered clauses and/or described throughout the present document.

20 The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather, the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without  
25 departing from the spirit and scope of the invention as set forth in the appended claims.

**Claims:**

1. A method of producing hydrogen, the method comprising:
  - 5 receiving a feed gas comprising hydrocarbons; and
  - performing reforming processes so as to generate hydrogen in dependence on the feed gas;
  - 10 wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and
  - heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;
  - 15 wherein the method is performed in a hydrogen production plant that is integrated with one or more further processing plants.
2. The method according to claim 1, further comprising:
  - 20 optionally saturating the received feed gas with at least water; and
  - pre-reforming the gas to generate a pre-reformed gas;
  - 25 wherein the reforming processes are performed on the pre-reformed gas.
3. The method according to claim 2, further comprising adding a hydrogen rich stream to the received feed gas before the feed gas is input to the pre-reforming process.
4. The method according to any preceding claim, further comprising:
  - 30 performing a water-gas-shift on the gas output from the reforming processes; and
  - separating hydrogen from the shifted gas.
  - 35
5. The method according to claim 4, further comprising compressing and, optionally, liquifying the separated hydrogen.

6. The method according to claim 4 or 5, further comprising separating carbon dioxide from the shifted gas.
- 5 7. The method according to claim 6, further comprising compressing and, optionally, liquifying the separated carbon dioxide.
8. The method according to any of claims 2 to 7, further comprising removing sulfur from the received feed gas prior to saturating the received feed gas with water.
- 10 9. The method according to claim 8, wherein ZnO is used to remove sulfur from the feed gas.
10. The method according to any preceding claim, wherein the feed gas is natural gas.
11. The method according to any of claims 1 to 9, wherein the feed gas is a hydrocarbon rich  
15 gaseous stream from, or within, an oil refinery and/or a petrochemical plant.
12. The method according to any preceding claim, wherein the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical  
20 plant.
13. The method according to any of claims 2 to 12, wherein the method is performed in a hydrogen production plant that is integrated with a methanol synthesis plant; and
- 25 one or both of saturating the received feed gas with water and pre-reforming the gas is performed by the methanol synthesis plant; and
- the method comprises supplying at least part of the feed gas that is saturated with water, and/or at least part of the pre-reformed gas, from the methanol synthesis plant to the  
30 hydrogen plant.
14. The method according to any of claims 3 to 13, wherein the hydrogen rich stream that is added to the feed gas is generated by a synthesis loop in a methanol synthesis plant.
- 35 15. The method according to any preceding claim, further comprising:
- supplying at least part of any product that is generated in the hydrogen production plant to at least one of the one or more of the further processing plants that the hydrogen

production plant is integrated with such that the supplied product can be used by the at least one of the one or more of the further processing plants; and/or

5 supplying at least part of any product that is generated in at least one of the one or more of the further processing plants that the hydrogen production plant is integrated with to the hydrogen production plant such that the supplied product can be used by the hydrogen production plant.

10 16. The method according to any preceding claim, wherein the temperature of gas output from the autothermal reforming process is in the range 900-1100 °C, and preferably between 1000 and 1050 °C.

15 17. The method according to any preceding claim, wherein the temperature of gas output from the gas-heated reformer is in the range 400-800 °C, and preferably 450-700 °C, and further preferably 500-600 °C.

18. The method according to any preceding claim, further comprising providing the autothermal reforming process with:

20 oxygen from an air separation unit such as a cryogenic air separation unit;

oxygen or oxygen enriched air from a membrane air separation unit; and/or

25 oxygen from a pressure or vacuum swing adsorption unit.

19. The method according to any preceding claim, wherein the autothermal reforming process is supplied with oxygen from an auxiliary air separation unit that is part of a methanol synthesis plant or a nitrogen production plant.

30 20. The method according to claim 4 or any claim dependent thereon, wherein the water-gas-shift is performed in both a high-temperature-shift reactor and a low-temperature shift reactor.

35 21. The method according to any of claims 4 to 19, wherein the water-gas-shift is performed in a single reactor.

22. The method according to claim 4 or any claim dependent thereon, wherein hydrogen is separated by one or more of a PSA unit, a membrane that is optionally a Pd-membrane and/or a membrane in which the permeate side of the membrane is flushed by steam.
- 5 23. The method according to claim 6 or any claim dependent thereon, wherein carbon dioxide is separated by cryogenic processes and/or a solvent that is optionally methanol.
24. The method according to claim 6 or any claim dependent thereon, wherein hydrogen and/or carbon dioxide is liquified using the excess cooling capacity of an auxiliary processing plant, wherein optionally the auxiliary processing plant is an air-separation plant  
10 and the excess cooling capacity is in the form of cold oxygen and/or nitrogen.
25. The method according to claim 4 or any claim dependent thereon, wherein the further processing plant is a methanol synthesis plant and all, or part of, the separated hydrogen is  
15 used to adjust the stoichiometric number of the methanol synthesis plant so that the stoichiometric number is 2.0 or slightly above 2.
26. The method according to claim 4 or any claim dependent thereon, wherein, in use, all, or part of, the separated hydrogen is used to reduce carbon dioxide emission from an  
20 auxiliary processing plant, optionally the hydrogen being added to burners of a fired heater and, optionally, the burners are part of a steam reformer.
27. The method according to claim 4 or any claim dependent thereon, wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and  
25 the method further comprises using at least part of the rest gas.
28. The method according to claim 27, wherein at least part of the rest gas is used as a fuel for  
30 one or more of:
- pre-heating one or more of the feed gas, the gas input to a pre-treatment process, the gas input to a pre-reforming process and the gas input to the gas-heated reforming process;
- generating steam for use in a pre-reforming process and/or for adding to the gas stream  
35 input to a water gas shift reactor; and
- powering a gas turbine.

29. The method according to claim 27 or 28, wherein at least part of the rest gas is fed into the autothermal reforming process and/or the gas-heated reforming process.
30. The method according to any preceding claim, wherein the hydrogen production plant is  
5 integrated with a methanol synthesis plant; and
- the product  $G \cdot H$  is at least 0.02, preferably above 0.05, more preferably above 0.1 and most preferably above 0.2;
- 10 wherein:
- $G$  is the natural gas consumption in the hydrogen plant relative to the methanol plant; and
- $H$  is the fraction of hydrogen produced by the hydrogen production plant that is directed to  
15 the methanol synthesis plant for consumption in burners therein.
31. A method of producing hydrogen, the method comprising:
- receiving a feed gas comprising hydrocarbons; and
- 20 performing reforming processes so as to generate hydrogen in dependence on the feed gas;
- wherein the reforming processes comprise both a gas-heated reforming process and an  
25 autothermal reforming process; and
- heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;
- 30 the method further comprising saturating the received feed gas with water; and
- pre-reforming the gas to generate pre-reformed gas;
- wherein the reforming processes are performed on the pre-reformed gas.
- 35 32. A method of producing hydrogen, the method comprising:
- receiving a feed gas comprising hydrocarbons; and

performing reforming processes so as to generate hydrogen in dependence on the feed gas;

wherein the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

the method further comprising:

performing a water-gas-shift on the gas output from the reforming processes; and

separating hydrogen from the shifted gas;

wherein the process of separating hydrogen from the shifted gas comprises generating a rest gas; and

the method further comprises using at least part of the rest gas.

33. A hydrogen production plant arranged to perform the method of claim 31 or claim 32.

34. A hydrogen production plant and one or more further processing plants arranged to perform the method of any of claims 1 to 32.

35. A hydrogen production plant and one or more further processing plants according to claim 34, wherein the one or more further processing plants include any of a methanol synthesis plant, a nitrogen production plant, a plant for Fischer-Tropsch synthesis, an oil refinery, an air-separation plant and a petrochemical plant.



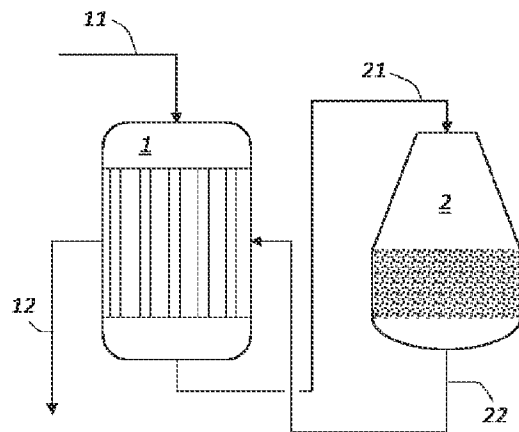


Figure 1

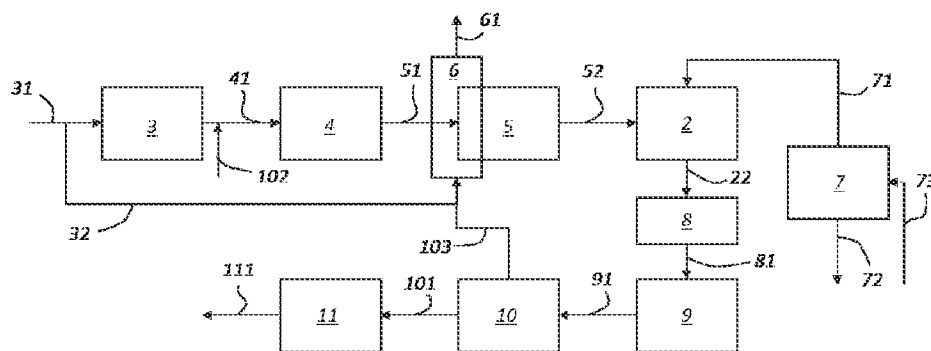


Figure 2

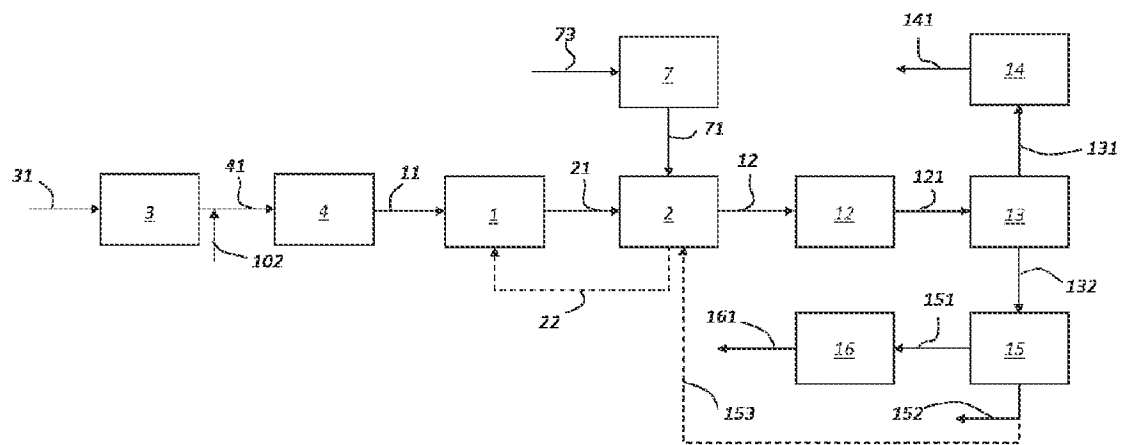


Figure 3

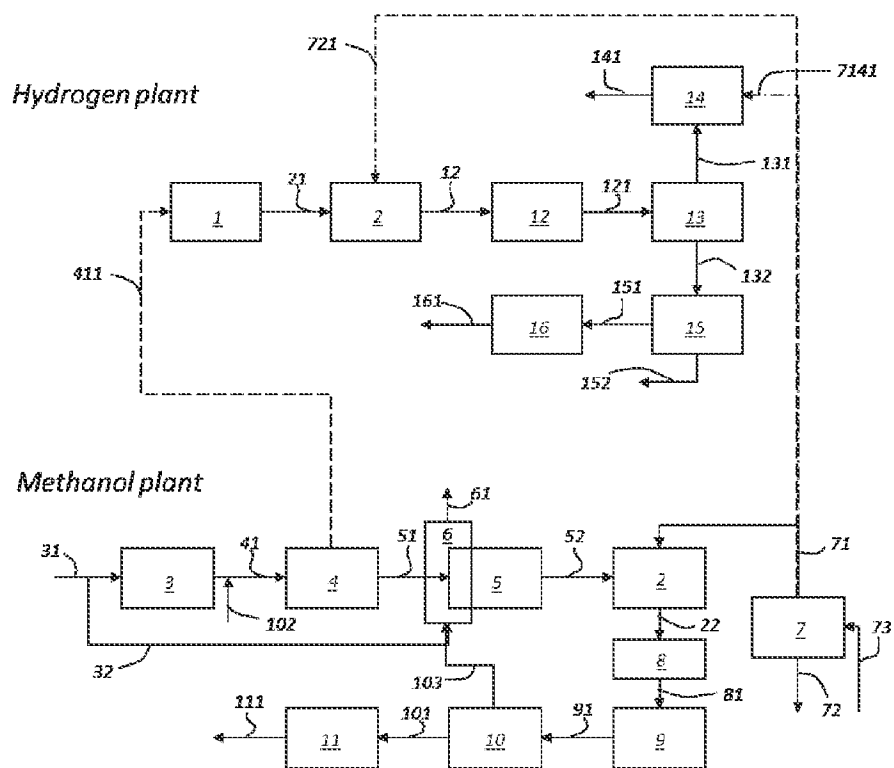


Figure 4

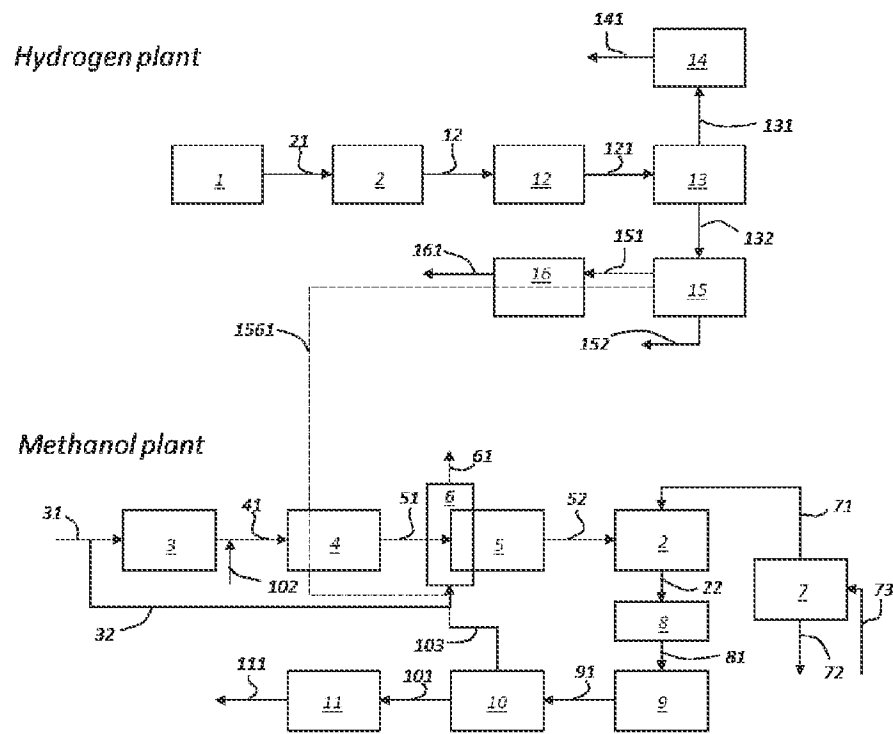


Figure 5

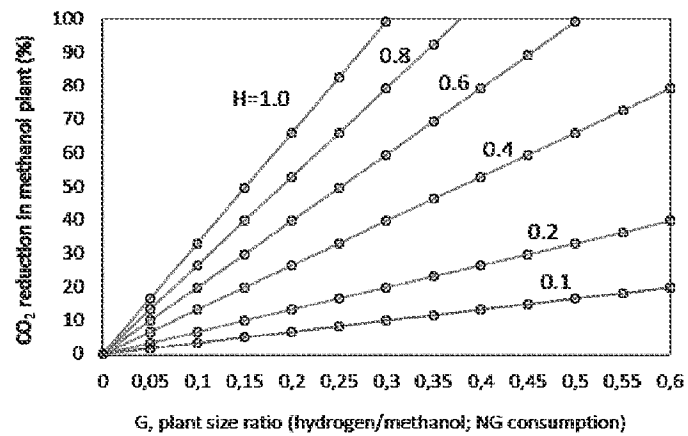


Figure 6

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/053986

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B3/38 C01B3/48  
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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                   | Relevant to claim No.                               |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|
| X         | <p>WO 2008/122399 A1 (SAUDI BASIC IND CORP [SA]; SABIC PETROCHEMICALS BV [NL]; AHMED IJAZ [S] 16 October 2008 (2008-10-16)</p> <p>abstract<br/>page 9, line 20 - page 10, line 11<br/>page 11, line 16 - page 12, line 10<br/>page 14, lines 18-19<br/>page 16, lines 5-10<br/>figures 1,2</p> <p>-----<br/>-/--</p> | <p>1-3,<br/>8-16, 19,<br/>25, 30,<br/>31, 33-35</p> |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

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

"S" document member of the same patent family

Date of the actual completion of the international search

15 March 2019

Date of mailing of the international search report

25/03/2019

Name and mailing address of the ISA/

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                 | Relevant to claim No.                                                       |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| X         | <p>WO 2011/150253 A1 (GTLPETROL LLC [US]; ALLAM RODNEY J [GB])<br/>1 December 2011 (2011-12-01)</p> <p>page 6, line 8 - page 7, line 29<br/>page 11, line 12 - page 12, line 15<br/>page 8, lines 25-27<br/>page 14, lines 16-25<br/>page 15, lines 6-11, 21-25<br/>page 20, lines 9-15<br/>figures 2,4</p>                                                        | <p>1,4-8,<br/>10,12,<br/>15,16,<br/>18,<br/>20-23,<br/>25-30,<br/>32-35</p> |
| X         | <p>WO 2014/072679 A1 (JOHNSON MATTHEY PLC [GB]) 15 May 2014 (2014-05-15)</p> <p>abstract<br/>claims 1,15<br/>page 2, lines 27-31<br/>page 3, lines 11-15<br/>page 4, lines 29-39<br/>page 5, lines 15,16,36,37<br/>page 6, lines 20-24<br/>page 7, lines 9-24</p>                                                                                                  | <p>1,2,8,<br/>10,<br/>12-17,<br/>19,25,<br/>30,31,<br/>33-35</p>            |
| X         | <p>WO 2011/077107 A1 (JOHNSON MATTHEY PLC [GB]; MCKENNA MARK [GB]; ABBOTT PETER EDWARD JAMES) 30 June 2011 (2011-06-30)</p> <p>abstract<br/>page 3, lines 5-14<br/>page 5, lines 12-15, 28-30<br/>page 6, lines 1-3, 31-33<br/>page 8, lines 13-16, 35-37<br/>page 9, lines 11-24<br/>page 12, line 6 - page 13, line 24<br/>figure 1<br/>claims 1,3,7,9,10,15</p> | <p>1,4-8,<br/>10,11,<br/>15-18,<br/>20-22,<br/>24,<br/>27-30,<br/>32-35</p> |
| X         | <p>US 2009/186952 A1 (STEYNBERG ANDRE PETER [ZA] ET AL) 23 July 2009 (2009-07-23)</p> <p>abstract<br/>paragraphs [0048] - [0062], [0070] - [0073]<br/>figures 1,2</p>                                                                                                                                                                                              | <p>1,2,10,<br/>12,31,<br/>33-35</p>                                         |

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/053986

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                         | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 2013/345324 A1 (KNUDSEN BJERG LARI [DK]<br>ET AL) 26 December 2013 (2013-12-26)<br>abstract<br>claims 1,3,5,11<br>----- | 1,10,12,<br>33-35     |

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/053986

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                                                                                                                                                                                          | Publication<br>date                                                                                                                                                                                                          |
|-------------------------------------------|---------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| WO 2008122399 A1                          | 16-10-2008          | AT 492511 T<br>DK 2142467 T3<br>EP 2142467 A1<br>ES 2357185 T3<br>WO 2008122399 A1                                                                                                                                                                                                                  | 15-01-2011<br>21-02-2011<br>13-01-2010<br>19-04-2011<br>16-10-2008                                                                                                                                                           |
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14 South Square  
Gray's Inn  
London  
Greater London WC1R 5JJ  
ROYAUME UNI

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT AND  
THE WRITTEN OPINION OF THE INTERNATIONAL  
SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

|                                                        |                                                        |                               |
|--------------------------------------------------------|--------------------------------------------------------|-------------------------------|
| Date of mailing<br>(day/month/year)                    |                                                        | 25 May 2021 (25-05-2021)      |
| Applicant's or agent's file reference<br>N418823WO HHG | <b>FOR FURTHER ACTION</b> See paragraphs 1 and 4 below |                               |
| International application No.<br>PCT/EP2021/054441     | International filing date<br>(day/month/year)          | 23 February 2021 (23-02-2021) |
| Applicant<br>REINERTSEN NEW ENERGY AS                  |                                                        |                               |

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

**When?** The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

**How?** Directly to the International Bureau preferably through ePCT, or on paper to:  
The International Bureau of WIPO, 34 chemin des Colombettes, 1211 Geneva 20, Switzerland

For more detailed instructions, see the *PCT Applicant's Guide*, International Phase, paragraphs 9.004 - 9.011.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.
3. ☐ With regard to any protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with any request to forward the texts of both the protest and the decision thereon to the designated Offices.
- ☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

**4. Reminders**

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. These comments will be made available to the public after international publication. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established.

Shortly after the expiration of 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau before the completion of the technical preparations for international publication (Rules 90bis.1 and 90bis.3).

Within 19 months from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later); otherwise, the applicant must, within 20 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices. In respect of other designated Offices, the time limit of 30 months (or later) will apply even if no demand is filed within 19 months. For details about the applicable time limits, Office by Office, see [www.wipo.int/pct/en/texts/time\\_limits.html](http://www.wipo.int/pct/en/texts/time_limits.html) and the *PCT Applicant's Guide*, National Chapters.

Within 22 months from the priority date, the applicant may request that a supplementary international search be carried out by a different International Searching Authority that offers this service (Rule 45bis.1). The procedure for requesting supplementary international search is described in the *PCT Applicant's Guide*, International Phase, paragraphs 8.006-8.032.

|                                                                                                                                                                                                               |                                               |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|
| Name and mailing address of the International Searching Authority                                                                                                                                             | Authorized officer                            |
|  European Patent Office, P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk<br>Tel. (+31-70) 340-2040<br>Fax: (+31-70) 340-3016 | SPREAFICO, Serena<br>Tel: +49 (0)89 2399-4773 |

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|                                                            |                                                                                                      |                                                                            |
|------------------------------------------------------------|------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Applicant's or agent's file reference<br><br>N418823WO HHG | <b>FOR FURTHER ACTION</b><br><br>see Form PCT/ISA/220<br>as well as, where applicable, item 5 below. |                                                                            |
| International application No.<br><br>PCT/EP2021/054441     | International filing date (day/month/year)<br><br>23 February 2021 (23-02-2021)                      | (Earliest) Priority Date (day/month/year)<br><br>6 March 2020 (06-03-2020) |
| Applicant<br><br>REINERTSEN NEW ENERGY AS                  |                                                                                                      |                                                                            |

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.

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

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

- ☒ the international application in the language in which it was filed  
☐ a translation of the international application into \_\_\_\_\_, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake**, authorized by or notified to this Authority under Rule 91 (Rule 43.6bis(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

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

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

4. With regard to the **title**,

- ☒ the text is approved as submitted by the applicant  
☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant  
☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,

- a. the figure of the **drawings** to be published with the abstract is Figure No. 9  
☒ 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/EP2021/054441

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B3/48 C01B3/50  
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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                     | Relevant to claim No.             |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|
| X         | WO 2019/162236 A1 (REINERTSEN NEW ENERGY AS [NO]) 29 August 2019 (2019-08-29)<br><br>abstract<br>claims 1,2,4,7,8,10,18,21-23,27,28<br>figure 2                                                                        | 1-8,<br>11-14,<br>19,21,<br>22,24 |
| X         | US 2010/310949 A1 (LICHT WILLIAM ROBERT [US] ET AL) 9 December 2010 (2010-12-09)<br><br>abstract<br>figure 2<br>claims 1,2<br>paragraphs [0023], [0036], [0047],<br>[0049], [0050], [0052], [0053]<br><br>-----<br>-/- | 1,2,5,7,<br>8,11,<br>15-19,24     |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

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

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

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

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

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

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

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

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

"Z" document member of the same patent family

Date of the actual completion of the international search

12 May 2021

Date of mailing of the international search report

25/05/2021

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

Authorized officer

Alvarez Rodriguez, C

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2021/054441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                      | Relevant to claim No.                                |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| X         | <p>US 2014/170052 A1 (IAQUANIELLO GAETANO [IT] ET AL) 19 June 2014 (2014-06-19)</p> <p>abstract<br/>claims 1,3,6,8,9,11<br/>figure 2<br/>paragraphs [0023], [0036], [0039] - [0044], [0061], [0062]</p> | <p>1,2,5,7,<br/>8,11,12,<br/>14-18,<br/>20,23-25</p> |
| X         | <p>US 8 715 617 B2 (GENKIN EUGENE S [US]; HERSHMAN PATRICIA KENTOSH [US] ET AL.) 6 May 2014 (2014-05-06)</p> <p>claims 1-3<br/>figure 2<br/>column 6 - column 10</p>                                    | <p>1,2,5,<br/>7-12,<br/>14-19,24</p>                 |
| X         | <p>US 6 090 312 A (ZIAKA ZOE D [US] ET AL) 18 July 2000 (2000-07-18)</p> <p>figure 1<br/>claims 1,4<br/>column 1, lines 7-23<br/>column 2, line 66 - column 3, line 32</p>                              | <p>1,8,11,<br/>12,<br/>17-19,24</p>                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/054441

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                | Publication<br>date                                                                            |
|-------------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| WO 2019162236 A1                          | 29-08-2019          | EP 3755655 A1<br>GB 2571136 A<br>WO 2019162236 A1                                                                         | 30-12-2020<br>21-08-2019<br>29-08-2019                                                         |
| US 2010310949 A1                          | 09-12-2010          | BR PI1001985 A2<br>CA 2705640 A1<br>CN 101905867 A<br>EP 2266922 A1<br>ES 2525532 T3<br>PL 2266922 T3<br>US 2010310949 A1 | 05-07-2011<br>03-12-2010<br>08-12-2010<br>29-12-2010<br>26-12-2014<br>30-06-2015<br>09-12-2010 |
| US 2014170052 A1                          | 19-06-2014          | CA 2835472 A1<br>CN 103648970 A<br>DK 2723676 T3<br>EP 2723676 A1<br>LT 2723676 T<br>US 2014170052 A1<br>WO 2012177137 A1 | 27-12-2012<br>19-03-2014<br>25-02-2019<br>30-04-2014<br>12-03-2019<br>19-06-2014<br>27-12-2012 |
| US 8715617 B2                             | 06-05-2014          | NONE                                                                                                                      |                                                                                                |
| US 6090312 A                              | 18-07-2000          | US 6090312 A<br>US 6919062 B1                                                                                             | 18-07-2000<br>19-07-2005                                                                       |

TITLE: HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

APPLICANT: REINERTSEN NEW ENERGY AS

IPC CLASSIFICATION: C01B3/48, C01B3/50

EXAMINER: Alvarez Rodriguez, C

CONSULTED DATABASES:

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC: C01B3/48, C01B3/50, C01B2203/0233, C01B2203/0244, C01B2203/0283, C01B2203/0405, C01B2203/0415, C01B2203/043, C01B2203/046, C01B2203/0475, C01B2203/0495, C01B2203/068, C01B2203/146, C01B2203/148

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:

Reforming

WGS, water gas shift

Hydrogen separation

Carbon dioxide separation/removal

Membrane

PSA, pressure swing adsorption

Recycle, recycling

Rest gas, tail gas, off-gas, waste gas

Ammonia

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

## PCT

### WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.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.  
PCT/EP2021/054441

International filing date (day/month/year)  
23.02.2021

Priority date (day/month/year)  
06.03.2020

International Patent Classification (IPC) or both national classification and IPC  
INV. C01B3/48 C01B3/50

Applicant  
REINERTSEN NEW ENERGY AS

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 43bis.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 notified the International Bureau under Rule 68.1 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:



European Patent Office  
D 80298 Munich  
Tel. +49 89 23393 - 0  
Fax: +49 89 23399 - 4465

Date of completion of  
this opinion

see form  
PCT/ISA/210

Authorized Officer

Alvarez Rodriguez, C  
Telephone No. +49 89 23399-0



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**Box No. I Basis of the opinion**

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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 43bis.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 13ter.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 13ter.1(a)).
    - ☐ on paper or in the form of an image file (Rule 13ter.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:



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

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1. Statement

|                               |             |             |
|-------------------------------|-------------|-------------|
| Novelty (N)                   | Yes: Claims |             |
|                               | No: Claims  | <u>1-25</u> |
| Inventive step (IS)           | Yes: Claims |             |
|                               | No: Claims  | <u>1-25</u> |
| Industrial applicability (IA) | Yes: Claims | <u>1-25</u> |
|                               | No: Claims  |             |

2. Citations and explanations

see separate sheet

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**Box No. VIII** Certain observations on the international application

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The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**Re Item V**

1 Reference is made to the following documents:

- D1: WO 2019/162236 A1 (REINERTSEN NEW ENERGY AS [NO]) 29 August 2019 (2019-08-29)
- D2: US 2010/310949 A1 (LICHT WILLIAM ROBERT [US] ET AL) 9 December 2010 (2010-12-09)
- D3: US 2014/170052 A1 (IAQUANIELLO GAETANO [IT] ET AL) 19 June 2014 (2014-06-19)
- D4: US 8 715 617 B2 (GENKIN EUGENE S [US]; HERSHMAN PATRICIA KENTOSH [US] ET AL.) 6 May 2014 (2014-05-06)
- D5: US 6 090 312 A (ZIAKA ZOE D [US] ET AL) 18 July 2000 (2000-07-18)

**Novelty - Article 33(2) PCT**

2 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1 to 25 is not new in the sense of Article 33(2) PCT.

2.1 Document D1 discloses [abstract; claims 1,2,4,7,8,10,18,21-23,27,28; figure 2] a method of producing hydrogen, the method comprising: performing reforming processes of a hydrocarbon stream, wherein the reforming process involves a gas heated reforming and an autothermal reformer; performing a water-gas-shift process on the reformed gas; performing a hydrogen separation process using a palladium membrane or a PSA and performing a carbon dioxide separation process e.g. by cryogenic separation, so that separate streams of hydrogen, carbon dioxide and a rest gas are generated; and recycling the rest gas back into one or more of the one or more reforming processes, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process. Optionally, the process comprises a pre-reforming step and a desulfurization step. The reforming processes are supplied with oxygen from an air separation unit. Water can be condensed after the shift step.

Hence, the subject-matter of claims 1 to 8, 11 to 14, 19, 21, 22 and 24 is not new in view of D1.

- 2.2 Document D2 discloses [abstract; figure 2; claims 1,2; paragraphs [0023], [0036], [0047], [0049], [0050], [0052], [0053]] a method of producing hydrogen, the method comprising: reforming a hydrocarbon feed in a tubular reformer followed by a secondary reforming reactor; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; separating carbon dioxide in a scrubbing unit to form a CO<sub>2</sub>-depleted stream; separating the CO<sub>2</sub>-depleted stream to form hydrogen and a by-product gas, e.g. in a pressure swing adsorption unit; introducing 50% to 98% of the by-product gas into the process stream at a location upstream of the plurality of catalyst-containing reformer tubes and/or into the reformat stream at a location upstream of a reforming catalyst in a secondary reforming reactor. The process stream can be natural gas and may be pre-reformed prior to entering the tubular reformer [0036]. The shift reaction takes place in one reactor at a temperature between 190°C and 300°C and using copper as catalyst [0023].

Hence, the subject-matter of claims 1, 2, 5, 7, 8, 11, 15 to 19 and 24 is not new in view of D2.

- 2.3 Document D3 discloses [abstract; claims 1, 3, 6, 8, 9,11; figure 2; paragraphs [0023], [0036], [0039] - [0044], [0061], [0062]] a process for producing ammonia comprising the steps of: (a) subjecting a hydrocarbon material to catalytic partial oxidation to produce a synthesis gas; (b) subjecting the synthesis gas to a WGS reaction; (c) removing CO<sub>2</sub> from the gas mixture; (d) purifying hydrogen using a pressure swing absorber after removing CO<sub>2</sub> to yield a pure hydrogen stream and a purge gas stream; and (e) reacting hydrogen with nitrogen to produce ammonia, wherein the purge gas stream is recycled to the hydrotreating reactor and then to the CPO reactor. The oxygen used in the catalytic partial oxidation and the nitrogen used in the ammonia-forming reaction are obtained from an air separation unit. The hydrocarbon material is selected from the group consisting of natural gas, Liquefied Petroleum Gas (LPG), refinery gas, naphtha, and mixtures thereof and can be pre-treated for removal of any impurities, such as sulphur compounds.

Hence, the content of claims 1, 2, 5, 7, 8, 11,12, 14 to 18, 20 and 23-25 is not new in view of D3.

- 2.4 D4 discloses [claims 1-3; figure 2; column 6 to column 10] a process for producing hydrogen comprising reforming a hydrocarbon feed in a first reactor, introducing oxygen and the reformat from the first reactor into a second reactor, shifting the reformat from the second reactor; removing water from the

shifted reformat; separating carbon dioxide and entering the remaining stream into a PSA to separate hydrogen that produces a tail stream wherein a portion of the tail gas is recycled to at least one of the first reactor and the second reactor and a second portion is recycled to the PSA. The process also comprise a pre-reforming step and a desulfurization step. The oxygen of the second reactor is provided by a air separation unit.

Hence, the subject-matter of claims 1, 2, 5, 7 to 12, 14 to 19 and 24 is not new in view of D4.

- 2.5 D5 discloses [figure 1; claims 1,4; column 1, lines 7-23; column 2, line 66 - column 3, line 32] a process that converts gaseous hydrocarbons via steam reforming and water gas shift reaction to hydrogen, carbon monoxide and carbon dioxide products with the hydrogen and carbon dioxide to be separated in downstream membrane permeators, consecutively placed after the reactors, and wherein the rest gas stream obtained in the membrane permeators is recycled to the inlet of the reformer. The process also comprises a steam condensation before the separation step.

Hence, the content of claims 1, 8, 11, 12, 17, 18, 19 and 24 is not new in view of D5.

### Re Item VIII

#### **Clarity - Article 6 PCT**

- 3 The present application is unclear for the following reasons:
- Claim 18 attempts to define the subject-matter in terms of the result to be achieved instead of providing the technical features needed to achieve said effect. Hence, claim 18 is unclear.
  - The hydrogen production plant of claim 24 and the ammonia production plant of claim 25 are not defined in term of their technical features and are therefore unclear.
  - The description renders the scope of the claims unclear, since embodiments 1 to 4 of the description, which correspond to figures 3 to 6, do not comprise the recycling of the rest gas and are not therefore according to the invention as defined in claim 1.

- The expressions "incorporated by reference" used in page 26, line 21 and "spirit of the invention" used in page 33, line 24 raise doubts about the scope of the invention.
- The claims-like clauses used in pages 20 to 33 raise doubts about the scope of the invention.

**Possible steps after receipt of the international search report (ISR) and written opinion of the International Searching Authority (WO/ISA)**

**General information**

For all international applications, the competent International Searching Authority (ISA) will establish an international search report (ISR) accompanied by a written opinion of the International Searching Authority (WO/ISA). The WO/ISA may be responded to by

- filing informal comments with the **International Bureau of WIPO (IB)** (where no demand for international preliminary examination (**demand**) is filed)
- filing amendments under Art. 19 PCT (this can be done whether or not a **demand** is filed)
- filing amendments under Art. 34 PCT and/or formal observations in response to objections raised in the **WO/ISA** (where a **demand** is actually filed)

This document explains these possibilities.

**Filing informal comments**

After receipt of the **ISR and WO/ISA**, the applicant may file informal comments on the **WO/ISA**, **directly with the IB** (see International Search and Preliminary Examination Guidelines 2.15). These will be communicated to the designated/elected Offices, together with the International Preliminary Report on Patentability (**IPRP**) at 30 months from the priority date.

**Amending claims under Art. 19 PCT**

The applicant may file **amended claims** under Art. 19 PCT, **directly with the IB** by the later of the following dates:

- 2 months from the date of mailing of the **ISR** and the **WO/ISA**
- 16 months from the priority date

**However**, any such amendment received by the **IB** after the expiration of the applicable time limit shall be **considered to have been received on time** by the **IB**, if it reaches it **before** the technical preparations for international publication have been completed (the 15th day prior to the date of publication, see PCT Applicant's Guide, International Phase, 9.013).

For further information, please see Rule 46 PCT as well as form PCT/ISA/220.

Please also note that, when filing amended claims under Art. 19 PCT, such amendments shall be **accompanied by a letter** identifying the amendments made and also the basis for the amendments in the application as originally filed (Rule 46.5(b) PCT). Where a **demand** is filed, failure to comply with this requirement may result in the amendments being ignored in the International Preliminary Examination Report (**IPER**), see Rule 70.2(c-bis) PCT.

**Filing a demand  
for international  
preliminary  
examination**

In principle, the **WO/ISA** will be considered to be the written opinion of the International Preliminary Examining Authority (**IPEA**). Where the **WO/ISA** issued by the **EPO** as **ISA** gives a positive opinion on the international application and the invention to which it relates, filing a demand with the **EPO** as **IPEA** would normally be unnecessary, since a positive **IPRP** would anyway be established by the **IB** based on the **WO/ISA** (see also further below).

If the applicant wishes to file a demand (for example, to allow him to argue his case in international preliminary examination with regard to objections raised in a negative **WO/ISA** before the **IPEA** issues an **IPER**), this must be done before expiration of **3 months after the date of mailing of the ISR and WO/ISA** or **22 months after priority date**, whichever expires later (Rule 54*bis* PCT). Amendments under Art. 34 PCT can be filed with the **IPEA**, normally at the same time as filing the demand (Rule 66.1(b) PCT) or within the time limit set for reply to any written opinion issued during international preliminary examination by the **IPEA**.

If a demand is filed at the **EPO** as **IPEA** and no comments/amendments have been received by the time the **EPO** starts drawing up the **IPER** (Rule 66.4*bis* PCT), the **WO/ISA** will be transformed by the **IPEA** into an **IPER** (also called the **IPRP (Chapter II)** which would merely reflect the content of the **WO/ISA** (OJ 10/2011, 532). The demand can still be withdrawn (Art. 37 PCT).

Please also note that, when filing amendments under Art. 34 PCT, such amendments shall be accompanied by a letter which identifies the amendments made and also the basis for the amendments in the application as originally filed (Rule 66.8(a) PCT). Failure to comply with this requirement may result in the amendments being ignored in the **IPER (IPRP (Chapter II))**, see Rule 70.2(c-*bis*) PCT.

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**Filing a request  
for supplementary  
international  
search**

The applicant may, with the **IB**, file a request for **supplementary international search** under Rule 45*bis*.1 PCT. The present **ISR** and **WO/ISA** may also be taken into account in the execution of that supplementary international search, provided that these are available to the Authority charged with this task before it starts the supplementary search (Rule 45*bis*.5 PCT).

This kind of request **cannot be filed specifying the ISA** who did the international search.

More information on this topic can be found in the **PCT Applicant's Guide**, Chapter 8 (<http://www.wipo.int/pct/en/guide/ip08.html>).

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**End of the  
international  
phase**

Where no demand is filed, at the end of the international phase, the **IB** will transform the **WO/ISA** into the **IPRP (PCT Chapter I)** (Rule 44*bis* PCT), which will then be transmitted together with possible informal comments to the designated Offices. Where a demand is filed, the **WO/ISA** is not transformed into an **IPRP (Chapter I)** by the **IB**, but rather the **IPEA** will establish an **IPER**, (the **IPER** is the same as the **IPRP (PCT Chapter II)**, see Rule 70.15 PCT).

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**PCT** WELTORGANISATION FÜR GEISTIGES EIGENTUM  
 Internationales Büro  
 INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE  
 INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                  |                                                                                                                                                           |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>(51) Internationale Patentklassifikation <sup>5</sup> :<br/><br/>C01B 3/38, 31/18</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <p><b>A1</b></p> | <p>(11) Internationale Veröffentlichungsnummer: <b>WO 91/12200</b></p> <p>(43) Internationales<br/>Veröffentlichungsdatum: 22. August 1991 (22.08.91)</p> |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>(21) Internationales Aktenzeichen: PCT/EP91/00288</p> <p>(22) Internationales Anmeldedatum: 14. Februar 1991 (14.02.91)</p> <p>(30) Prioritätsdaten:<br/>P 40 04 869.1      16. Februar 1990 (16.02.90)    DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): L. &amp; C. STEINMÜLLER GMBH [DE/DE]; Postfach 10 08 55/65, D-5270 Gummersbach 1 (DE).</p> <p>(72) Erfinder; und<br/>(73) Erfinder/Anmelder (nur für US) : CZIMCZIK, Arno [DE/DE]; Ferndorfer Str. 90, D-5910 Kreuztal 4 (DE). SCHMITZ-GOEB, Manfred [DE/DE]; Lebrechtstr. 1, D-5270 Gummersbach (DE). FRIESE, Eckhard [DE/DE]; Frankengasse 16, D-5485 Sinzig-Koisdorf (DE).</p> </div> <div style="width: 48%;"> <p>(74) Anwalt: CARSTENS, Wilhelm; L. &amp; C. Steinmüller GmbH, Postfach 10 08 55/65, D-5270 Gummersbach 1 (DE).</p> <p>(81) Bestimmungsstaaten: AT (europäisches Patent), BE (europäisches Patent), CA, CH (europäisches Patent), DE (europäisches Patent), DK (europäisches Patent), ES (europäisches Patent), FR (europäisches Patent), GB (europäisches Patent), GR (europäisches Patent), IT (europäisches Patent), LU (europäisches Patent), NL (europäisches Patent), NO, SE (europäisches Patent), US.</p> <p>Veröffentlicht<br/>Mit internationalem Recherchenbericht.<br/>Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist, Veröffentlichung wird wiederholt falls Änderungen eintreffen.</p> </div> </div>                                                            |                  |                                                                                                                                                           |
| <p>(54) Title: PROCESS FOR GENERATING CARBON MONOXIDE</p> <p>(54) Bezeichnung: VERFAHREN ZUR ERZEUGUNG VON KOHLENMONOXID</p> <p>(57) Abstract</p> <p>According to the invention, in a process for generating carbon monoxide in which a mixture of a hydrocarbon, preferably methane, and carbon dioxide is supplied in the presence of a catalyst with the provision of heat to at least one reformation stage and carbon dioxide and hydrogen are separated from the reformed initial gas mixture, the gas mixture is taken to a convectively heated first reformation stage, the exhaust gas from the first reformation stage is taken together with oxygen to an autothermal second reformation stage and the exhaust gas from the second reformation stage is taken to the convectively heated reformation stage as the heating gas.</p> <p>(57) Zusammenfassung</p> <p>Bei einem Verfahren zur Erzeugung von Kohlenmonoxid, bei dem ein Gemisch aus Kohlenwasserstoff, vorzugsweise Methan, und Kohlendioxid in Gegenwart eines Katalysators unter Zufuhr von Wärme mindestens einer Reformierstufe zugeführt wird und Kohlendioxid und Wasserstoff aus dem reformierten Ausgangsgasgemisch abgetrennt werden, ist erfindungsgemäß vorgesehen, daß das Gasgemisch einer konvektiv beheizten ersten Reformierstufe zugeführt wird, das Ausgangsgas der ersten Reformierstufe zusammen mit Sauerstoff einer autothermen zweiten Reformierstufe zugeführt wird, und das Ausgangsgas der zweiten Reformierstufe der konvektiv beheizten Reformierstufe als Heizgas zugeführt wird.</p> |                  |                                                                                                                                                           |



# **LEDIGLICH ZUR INFORMATION**

Code, die zur Identifizierung von PCT-Vertragsstaaten auf den Kopfbögen der Schriften, die internationale Anmeldungen gemäss dem PCT veröffentlichen.

|    |                                |    |                                   |    |                                |
|----|--------------------------------|----|-----------------------------------|----|--------------------------------|
| AT | Österreich                     | ES | Spanien                           | ML | Mali                           |
| AU | Australien                     | FI | Finnland                          | MN | Mongolei                       |
| BB | Barbados                       | FR | Frankreich                        | MR | Mauritanien                    |
| BE | Belgien                        | GA | Gabon                             | MW | Malawi                         |
| BF | Burkina Faso                   | GB | Vereinigtes Königreich            | NL | Niederlande                    |
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| CH | Schweiz                        | KR | Republik Korea                    | SU | Sowjet Union                   |
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| CM | Kamerun                        | LK | Sri Lanka                         | TG | Togo                           |
| CS | Tschechoslowakei               | LU | Luxemburg                         | US | Vereinigte Staaten von Amerika |
| DE | Deutschland                    | MC | Monaco                            |    |                                |
| DK | Dänemark                       | MG | Madagaskar                        |    |                                |

## Beschreibung

### Verfahren zur Erzeugung von Kohlenmonoxid

Die Erfindung betrifft ein Verfahren zur Erzeugung von Kohlenmonoxid, bei dem ein Gemisch aus Kohlenwasserstoff, vorzugsweise Methan, und Kohlendioxid in Gegenwart eines Katalysators unter Zufuhr von Wärme mindestens einer Reformierstufe zugeführt wird und Kohlendioxid und Wasserstoff aus dem reformierten Ausgangsgasgemisch abgetrennt werden.

Aus der DE-Z. Chem.-Ing.-Tech. 51 (1979) Nr. 11, Seiten 1079-1098, insbesondere Seite 1088 ist ein solches Verfahren bekannt. Die Reformierstufe besteht aus einem Strahlungsreformer, dem Verbrennungsluft und Brennstoff zum Beheizen zugeführt werden. Der Kohlendioxidanteil aus den Abgasen der Reformerbeheizung wird ebenso wie der im Produktgas verbleibende Kohlendioxid-Restanteil über eine Wäsche für den Reformierungsprozeß zurückgewonnen. Der Stickstoff-Anteil aus den Abgasen wird als Nebenprodukt abgeführt.

Dem Reformierprozeß wird an verschiedenen Stellen durch Kühler Wärme entzogen.

Es ist daher die Aufgabe der vorliegenden Erfindung, ein Verfahren der im Oberbegriff genannten Art anzugeben, bei

dem die erzeugte Wärme allein für das Reformierverfahren selbst genutzt wird.

Diese Aufgabe wird dadurch gelöst, daß das Gasgemisch einer konvektiv beheizten ersten Reformierstufe zugeführt wird, das Ausgangsgas der ersten Reformierstufe zusammen mit Sauerstoff einer autothermen zweiten Reformierstufe zugeführt wird, und das Ausgangsgas der zweiten Reformierstufe der konvektiv beheizten Reformierstufe als Heizgas zugeführt wird.

Die in der autothermen Reformierstufe erzeugte Wärme wird für das Verfahren selbst genutzt, da sie über das Heizgas zum Beheizen der ersten Reformierstufe verwendet wird.

Konvektiv beheizte Reformierstufen sind an sich bekannt. Sie weisen vorzugsweise eine Vielzahl von Spaltrohren mit einem von einem Heizgas umspülten Außenrohr und einem der Gasrückführung dienenden Innenrohr auf, wobei der Raum zwischen dem Außenrohr und Innenrohr mit einem Katalysator gefüllt ist (vgl. z. B. Prospekt der Anmelderin: "Anlagen- und Apparatebau - Komponenten und Teilkreisläufe" (1986) Seite 31).

Autothermreformer, die oft als Sekundärreformer eingesetzt werden, sind auch an sich bekannt. Bei der  $\text{NH}_3$ -Synthese wird z. B. zunächst das Einsatzgas in einem Primärreformer einem Dampfreformierprozeß unterzogen. Das Ausgangsgas aus dem Primärreformer mit einem verhältnismäßig hohen Restgehalt an Methan wird dann in einem als Sekundärreformer dienenden Autothermreformer über eine Mischvorrichtung (Brenner) mit Luft gemischt und anschließend über eine Schüttung aus Katalysator geführt. Hier dient die Sekundärreformstufe dem Einbringen von Stickstoff in das Synthesegas (vgl. DE-Z. "Chemiker-Zeitung" (1972) Seite 141, rechte Spalte).

Um die Kohlenmonoxid-Ausbeute zu erhöhen ist es von Vorteil, wenn der zweiten Reformierstufe zusätzlich Kohlendioxid zugeführt wird.

Auch ist es möglich, der zweiten Reformierstufe zusätzlich Kohlenwasserstoff zuzuführen, um eventuell die in der zweiten Reformierstufe erzeugte Wärmemenge zu erhöhen.

Wie bei dem bekannten Verfahren zur Erzeugung von Kohlenmonoxid ist es zweckmäßig, das aus dem Ausgangsgas der zweiten Reformierstufe abgetrennte Kohlendioxid als Rückführgas zu verwenden, d. h. der ersten und/oder der zweiten Reformierstufe zurückzuführen. Dasselbe gilt für den abgetrennten Wasserstoff.

Sollte der Wärmeinhalt der aus der konvektiv beheizten Reformierstufe austretenden Gase noch ausreichend groß sein, ist es zweckmäßig, mindestens eines der Einsatzgase und/oder mindestens eines der Rückführgase durch Wärmetausch mit dem Ausgangsgas der zweiten Reformierstufe vorzuwärmen, d. h. auch die verbleibende Abwärme in das Verfahren zur Herstellung von Kohlenmonoxid einzubinden und nicht wie bei der bekannten Verfahrensführung in externe Prozesse, z. B. zur Dampferzeugung.

Das erfindungsgemäße Verfahren soll nun anhand der beigefügten Figur näher erläutert werden.

Ein Gemisch aus im wesentlichen Methan ( $\text{CH}_4$ ) und Kohlendioxid ( $\text{CO}_2$ ) wird über Leitung 1, in der ein Wärmetauscher 2 angeordnet ist, einem konvektiv beheizten Reformier 3 zugeführt. In diesem durchströmt das vorgewärmte Gasgemisch mit einem Katalysator gefüllte Spaltrohre. Das Ausgangsgas des Reformers 3 mit hohen Anteilen an Kohlenmonoxid, Kohlendioxid, Wasserdampf und Wasserstoff, sowie einem Restgehalt an Methan wird über Leitung 4 einem Autothermreformer 5 zugeführt. Dem Autothermreformer 5 wird

Über eine Leitung 7 Sauerstoff ( $O_2$ ) zugeführt. Das über Leitung 4 zugeführte Ausgangsgas des Reformers 3 wird hier in einem autothermen Vorgang weiter reformiert, um den Restgehalt an Methan wesentlich zu verringern. Das Ausgangsgas des Autothermreformers 5 wird über eine Leitung 8 als Heizgas dem konvektiv beheizten Reformer 3 zugeleitet, in dem es die Spaltrohre von außen umströmt.

Das Ausgangsgas des Reformers 3 wird über eine Leitung 9, in der der Wärmetauscher 2 und ein weiterer Wärmetauscher 6 angeordnet sind, einem Wasserdampfabscheider 10 zugeführt, aus dem das abgeschiedene Wasser über eine Leitung 11 abgezogen wird. Das nunmehr aus einer Mischung von Kohlenmonoxid, Kohlendioxid und Wasserstoff und gegebenenfalls noch einem sehr geringen Anteil von Restmethan bestehende Synthesegas wird dann über Leitung 12 einer Kohlendioxidwäsche 13 zugeleitet. Das ausgewaschene Kohlendioxid wird über eine Leitung 14 als Rückführgas zur Leitung 1 zurückgeführt und/oder über eine über den Wärmetauscher 6 geführte Leitung 15 der Leitung 4 und damit dem Autothermreformer 5 zugeführt.

Das vom Kohlendioxid befreite Gas wird über eine Leitung 16 einer Wasserstoffabtrennung 17 zugeführt; das vom Wasserstoff befreite Gas wird als Produktgas über Leitung 18 abgezogen.

Der abgetrennte Wasserstoff kann über Leitungen 19 und 20 als Rückführgas den Reformern 3 bzw. 5 zugeführt werden. Der in der Figur gestrichelt dargestellte Wärmetauscher 21 soll zeigen, daß bei Bedarf auch eine Vorwärmung des rückgeführten Wasserstoffes durch das Ausgangsgas der ersten Reformierstufe in Betracht gezogen werden könnte.

Obwohl das Endprodukt des Verfahrens ein möglichst reines Kohlenmonoxid sein soll, ist mit Hilfe der Gasreinigungsstufen 10, 13 und 17 eine Einstellung eines im

wesentlichen Kohlenmonoxid enthaltenden Produktgases mit gewünschten Anteilen an Wasserdampf, Kohlendioxid und Wasserstoff möglich. Über eine Leitung 22 kann bei Bedarf auch dem Autothermreformer 5 Methan zugeführt werden, das zusammen mit dem Kohlendioxid im Wärmetauscher 6 vorgewärmt wird.

Durch die Direktheizung im Autothermreformer 5 und die konvektive Beheizung des Reformers 3 kommt es zu keiner Erzeugung von Rauchgas. Die Wärmezufuhr zum Reformer 3 erfolgt auf hohem Temperaturniveau, und die Wärme nach der Reformierstufe 3 fällt bei niedrigen Temperaturen an und kann durch Wärmetausch mit den Einsatz- bzw. Rückführgasen noch in den Prozeß eingebunden werden. Die Einsatzgase werden druckaufgeladen zugeführt, so daß es bei gleichem Druckverlust zu einer Prozeßführung mit besseren Wärmezufuhr- und Wärmeübergangsbedingungen kommt.

Die vorstehend beschriebenen Leitungsführungen dienen nur der Erläuterung des Verfahrensablaufes, so können z. B. die Leitungen 15 und 22 ohne vorherige Verbindung getrennt in die Leitung 4 einmünden oder auch als getrennte Leitungen zum Reformer 5 geführt werden, oder es kann z. B. die Leitung 19 direkt zum Reformer 3 geführt werden, ohne zuvor in die Leitung 1 einzumünden. Es kommt nur darauf an, daß die Einsatzgase, Ausgangsgase und Rückführgase den einzelnen Verfahrensstufen zur Erreichung des erfinderischen Zieles zugeführt werden.

(Hierzu 1 Blatt Zeichnungen)

### Patentansprüche

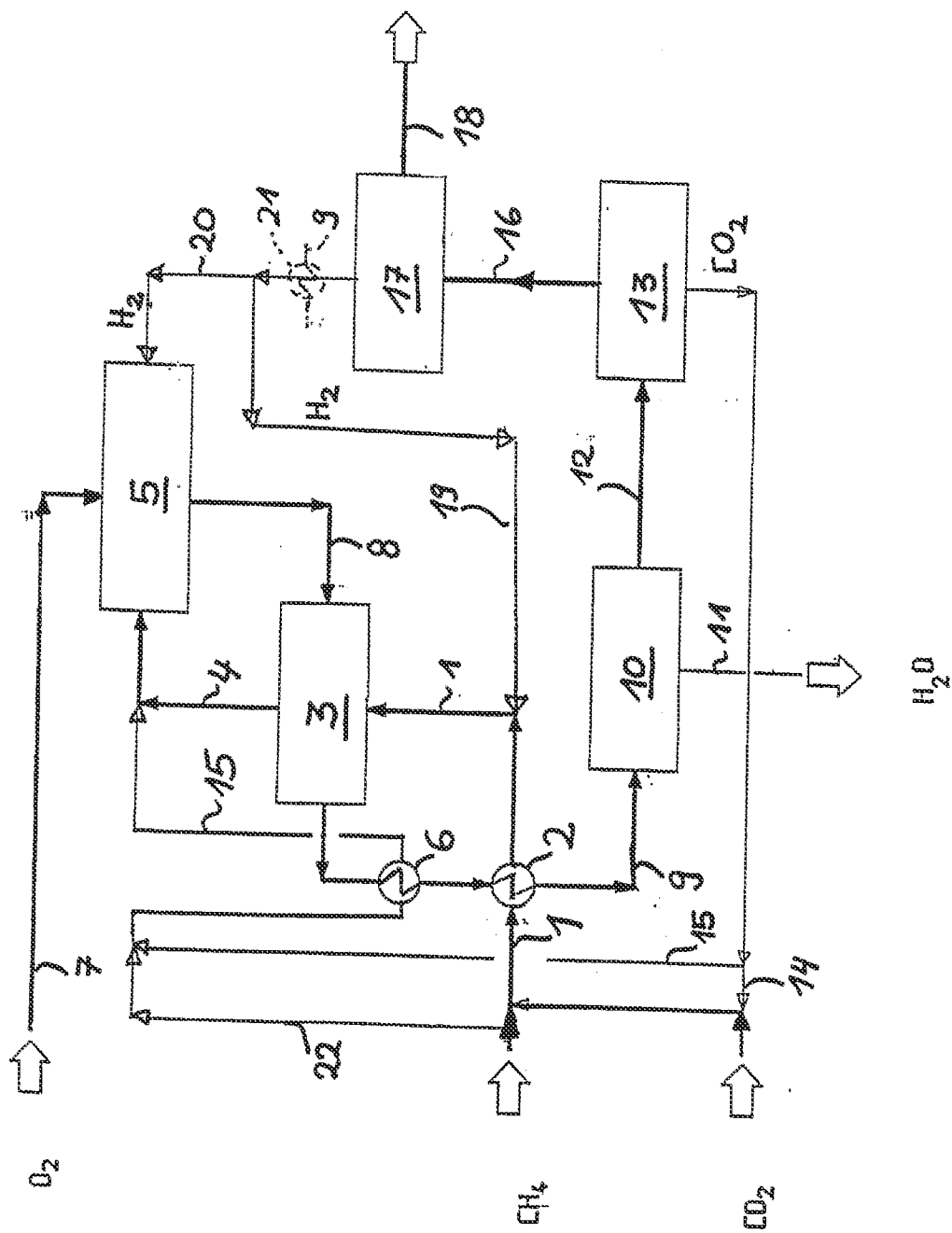
1. Verfahren zur Erzeugung von Kohlenmonoxid, bei dem ein Gemisch aus Kohlenwasserstoff, vorzugsweise Methan, und Kohlendioxid in Gegenwart eines Katalysators unter Zufuhr von Wärme mindestens einer Reformierstufe zugeführt wird und Kohlendioxid und Wasserstoff aus dem reformierten Ausgangsgasgemisch abgetrennt werden, d a d u r c h g e k e n n z e i c h n e t , daß das Gasgemisch einer konvektiv beheizten ersten Reformierstufe zugeführt wird, das Ausgangsgas der ersten Reformierstufe zusammen mit Sauerstoff einer autothermen zweiten Reformierstufe zugeführt wird, und das Ausgangsgas der zweiten Reformierstufe der konvektiv beheizten Reformierstufe als Heizgas zugeführt wird.
2. Verfahren nach Anspruch 1, d a d u r c h g e k e n n z e i c h n e t , daß der zweiten Reformierstufe zusätzlich Kohlendioxid zugeführt wird.
3. Verfahren nach Anspruch 1 oder 2, d a d u r c h g e k e n n z e i c h n e t , daß der zweiten Reformierstufe zusätzlich Kohlenwasserstoff zugeführt wird.
4. Verfahren nach mindestens einem der Ansprüche 1 bis 3, d a d u r c h g e k e n n z e i c h n e t , daß das

abgetrennte Kohlendioxid als Rückführgas verwendet wird.

5. Verfahren nach mindestens einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß der abgetrennte Wasserstoff als Rückführgas verwendet wird.
6. Verfahren nach mindestens einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß mindestens eines der Einsatzgase und/oder mindestens eines der Rückführgase durch Wärmetausch mit dem Ausgangsgas der zweiten Reformierstufe vorgewärmt wird.



CO 1/1



# INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/00288

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                              |                                     |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                              |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                              |                                     |
| Int.Cl. <sup>5</sup> C 01 B 3/38; C 01 B 31/18                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                              |                                     |
| <b>II. FIELDS SEARCHED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                              |                                     |
| Minimum Documentation Searched <sup>7</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                              |                                     |
| Classification System                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Classification Symbols                                                                                                                                                                                                                       |                                     |
| Int.Cl. <sup>5</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | C 01 B                                                                                                                                                                                                                                       |                                     |
| Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                              |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>9</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                              |                                     |
| Category *                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>                                                                                                                               | Relevant to Claim No. <sup>13</sup> |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | EP, A, 307843 (AIR PRODUCTS AND CHEMICALS )<br>22 March 1989, see page 4, line 35 - page 5, line 18; figure 2                                                                                                                                | 1                                   |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | ----                                                                                                                                                                                                                                         | 4,6                                 |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | EP, A, 194067 (ICI) 10 September 1986, see page 21, line 4 - page 22, line 12; claims 1-4; figure 8                                                                                                                                          | 1                                   |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | -----<br>CHEMIE. INGENIEUR. TECHNIK. vol. 51, No. 11, 1979, WEINHEIM DE pages 1079-1098; G. Schmitt: "Chemische Verfahren" see page 1088, right-hand column, lines 8-34; figure 8 (cited in the application)                                 | 1,4                                 |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | -----<br>CHEMIKER-ZEITUNG. 96 annual set No. 3, 1972, HEIDELBERG DE, pages 135-153; M. Appl et al.: "Herstellung von Synthesegas nach dem Steam-Reforming-Verfahren" see page 141, right-hand column, paragraph 2 (cited in the application) | 1                                   |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | -----<br>US, A, 3549335 (B.J. GROTZ, JR.) 22 December 1970<br>./....                                                                                                                                                                         |                                     |
| <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"Δ" document member of the same patent family</p> |                                                                                                                                                                                                                                              |                                     |
| <b>IV. CERTIFICATION</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                              |                                     |
| Date of the Actual Completion of the International Search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Date of Mailing of this International Search Report                                                                                                                                                                                          |                                     |
| 31 May 1991 (31.05.91)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 12 July 1991 (12.07.91)                                                                                                                                                                                                                      |                                     |
| International Searching Authority                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Signature of Authorized Officer                                                                                                                                                                                                              |                                     |
| European Patent Office                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                              |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |                                                                                    |                      |
|----------------------------------------------------------------------------|------------------------------------------------------------------------------------|----------------------|
| Category *                                                                 | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No |
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|                                                                            | ----                                                                               |                      |
| A                                                                          | DE, A, 3501459 (LINDE AG) 17 July 1986<br>-----                                    |                      |

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

PCT/EP 91/00288  
SA 44435

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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31/05/91

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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PCT/EP 91/00288

Internationaler Aktenzeichen

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|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|
| <b>I. KLASSEFIZIKATION DES ANMELDUNGS-GEGENSTANDS</b> (bei mehreren Klassifikations-sym-holen sind alle anzugeben) <sup>6</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                           |                                  |
| Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                           |                                  |
| Int.Kl. 5 C01B3/38 ; C01B31/18                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                           |                                  |
| <b>II. RECHERCHIERTE SACHGEBIETE</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                           |                                  |
| Recherchierte Mindestprüfstoff <sup>7</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                           |                                  |
| Klassifikationssystem                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Klassifikations-symbole                                                                                                                                                                                                   |                                  |
| Int.Kl. 5                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | C01B                                                                                                                                                                                                                      |                                  |
| Recherchierte nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Sachgebiete fallen <sup>8</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                           |                                  |
| <b>III. EINSCHLAGIGE VERÖFFENTLICHUNGEN<sup>9</sup></b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                           |                                  |
| Art. <sup>9</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Kennzeichnung der Veröffentlichung <sup>11</sup> , soweit erforderlich unter Angabe der maßgeblichen Teile <sup>12</sup>                                                                                                  | Betr. Anspruch Nr. <sup>13</sup> |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | EP,A,307843 (AIR PRODUCTS AND CHEMICALS)<br>22 März 1989<br>siehe Seite 4, Zeile 35 - Seite 5, Zeile 18;<br>Figur 2                                                                                                       | 1                                |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | ----                                                                                                                                                                                                                      | 4, 6                             |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | EP,A,194067 (ICI) 10 September 1986<br>siehe Seite 21, Zeile 4 - Seite 22, Zeile 12;<br>Ansprüche 1-4; Figur 8                                                                                                            | 1                                |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | ----                                                                                                                                                                                                                      | 1, 4                             |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | CHEMIE. INGENIEUR. TECHNIK.<br>vol. 51, no. 11, 1979, WEINHEIM DE<br>Seiten 1079 - 1098; G. Schmitt:<br>"Chemische Verfahren"<br>siehe Seite 1088, rechte Spalte, Zeilen 8 - 34;<br>Figur 8<br>(in der Anmeldung erwähnt) |                                  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | ----                                                                                                                                                                                                                      |                                  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | -/--                                                                                                                                                                                                                      |                                  |
| <p><sup>10</sup> Besondere Kategorien von angegebenen Veröffentlichungen:</p> <p>"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist</p> <p>"E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist</p> <p>"I" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)</p> <p>"O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht</p> <p>"P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist</p> <p>"T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angeht</p> <p>"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden</p> <p>"Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist</p> <p>"&amp;" Veröffentlichung, die Mitglied derselben Patentfamilie ist</p> |                                                                                                                                                                                                                           |                                  |
| <b>IV. BESCHEINIGUNG</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                           |                                  |
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| 31. MAI 1991                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 12. 07. 91                                                                                                                                                                                                                |                                  |
| Internationale Recherchenbehörde                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Unterschrift des bevollmächtigten Beauftragten                                                                                                                                                                            |                                  |
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Formblatt PCT/ISA/210 (Übers. 2) (Januar 1985)

| III. EINSCHLAGIGE VERÖFFENTLICHUNGEN (Fortsetzung von Blatt 2) |                                                                                                                                                                                                                                                                |                    |
|----------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
| Art °                                                          | Kennzeichnung der Veröffentlichung, soweit erforderlich unter Angabe der maßgeblichen Teile                                                                                                                                                                    | Betr. Anspruch Nr. |
| A                                                              | CHEMIKER-ZEITUNG.<br>96. Jahrgang<br>no. 3, 1972, HEIDELBERG DE<br>Seiten 135 - 153; M. Appl et al.:<br>"Herstellung von Synthesegas nach dem<br>Steam-Reforming-Verfahren"<br>siehe Seite 141, rechte Spalte, Absatz 2<br>(in der Anmeldung erwähnt)<br>----- | 1                  |
| A                                                              | US,A,3549335 (B.J. GROTZ, JR.) 22 Dezember 1970<br>-----                                                                                                                                                                                                       |                    |
| A                                                              | FR,A,2274672 (STONE & WEBSTER ENGINEERING CO.)<br>09 Januar 1976<br>-----                                                                                                                                                                                      |                    |
| A                                                              | DE,A,3501459 (LINDE AG) 17 Juli 1986<br>-----                                                                                                                                                                                                                  |                    |

# ANHANG ZUM INTERNATIONALEN RECHERCHENBERICHT ÜBER DIE INTERNATIONALE PATENTANMELDUNG NR.

PCT/EP 91/00288

SA 44435

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben.

Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am 31/05/91.

31/05/91

| Im Recherchenbericht<br>angeführtes Patentdokument | Datum der<br>Veröffentlichung | Mitglied(er) der<br>Patentfamilie | Datum der<br>Veröffentlichung |
|----------------------------------------------------|-------------------------------|-----------------------------------|-------------------------------|
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| DE-A-3501459                                       | 17-07-86                      | Keine                             |                               |

EPO FORM P8673

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82

### Process for generating carbon monoxide

#### Abstract

According to the invention, in a process for generating carbon monoxide in which a mixture of a hydrocarbon, preferably methane, and carbon dioxide is supplied in the presence of a catalyst with the provision of heat to at least one reformation stage and carbon dioxide and hydrogen are separated from the reformed initial gas mixture, the gas mixture is taken to a convectively heated first reformation stage, the exhaust gas from the first reformation stage is taken together with oxygen to an autothermal second reformation stage and the exhaust gas from the second reformation stage is taken to the convectively heated reformation stage as the heating gas.

#### Description

##### Process for the production of carbon monoxide

The invention relates to a process for the production of carbon monoxide, in which a mixture of hydrocarbon, preferably methane, and carbon dioxide is fed in the presence of a catalyst with the supply of heat to at least one reforming stage and carbon dioxide and hydrogen are separated from the reformed starting gas mixture.

From the DE-Z. Chem.-Ing.-Tech. 51 (1979) No. 11, pages 1079-1098, in particular page 1088, such a method is known. The reforming stage consists of a radiation reformer to which combustion air and fuel are fed for heating. The carbon dioxide content from the exhaust gases from the reformer heating is recovered for the reforming process, as is the residual carbon dioxide content remaining in the product gas. The nitrogen content from the exhaust gases is removed as a by-product.

Heat is removed from the reforming process at various points by coolers.

It is therefore the object of the present invention to specify a method of the type mentioned in the preamble which the heat generated is used solely for the reforming process itself.

This object is achieved in that the gas mixture is fed to a convectively heated first reforming stage, the starting gas of the first reforming stage is fed together with oxygen to an autothermal second reforming stage, and the starting gas of the second reforming stage is fed to the convectively heated reforming stage as heating gas.

The heat generated in the autothermal reforming stage is used for the process itself, since it is used to heat the first reforming stage via the heating gas.



Convectionally heated reforming stages are known per se. They preferably have a large number of canned tubes with an outer tube flushed with a heating gas and an inner tube serving for gas recirculation, the space between the outer tube and inner tube being filled with a catalyst (cf., for example, the applicant's prospectus: "Plant and Apparatus construction - components and circuits!" (1986) page 31).

Autothermal reformers, which are often used as secondary reformers, are also known per se. In the  $\text{NH}_3$  synthesis z. B. first subjected to a steam refoirer process the feed gas in a primary reformer. The starting gas from the primary reformer with a relatively high residual methane content is then mixed with air in an autothermal reformer serving as a secondary reformer via a mixing device (burner) and then passed over a bed of catalyst. Here, the secondary reform stage serves to introduce nitrogen into the synthesis gas (see DE-Z. "Chemiker-Zeitung" (1972) page 141, right column). In order to increase the carbon monoxide yield, it is advantageous if the second reforming stage is additionally supplied with carbon dioxide.

It is also possible to additionally supply hydrocarbon to the second reforming stage in order to possibly increase the amount of heat generated in the second reforming stage.

As with the known process for producing carbon monoxide, it is expedient to use the carbon dioxide separated from the starting gas of the second reforming stage as the recycle gas, i.e. H. the first and / or the second reforming stage. The same applies to the separated hydrogen.

If the heat content of the gases emerging from the convectively heated reforming stage is still sufficiently large, it is expedient to preheat at least one of the feed gases and / or at least one of the return gases by heat exchange with the starting gas of the second reforming stage, i.e. H. also to integrate the remaining waste heat in the process for the production of carbon monoxide un as in the known process management in external processes, for. B. for steam generation.

The method according to the invention will now be explained in more detail with reference to the attached figure.

A mixture of essentially methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) is fed via line 1, in which a heat exchanger 2 is arranged, to a convectively heated reformer 3. The preheated gas mixture flows through a can filled with a catalyst. The starting gas of the reformer 3 with high proportions of carbon monoxide, carbon dioxide, water vapor and hydrogen, and a residual methane content is fed via line 4 to an autothermal reformer 5. The autothermal reformer 5 we Via a line 7 oxygen ( $\text{O}_2$ ) supplied. The output gas of the reformer 3 supplied via line 4 is further reformed here in an autothermal process in order to substantially reduce the residual methane content. The starting gas of the autothermal reformer 5 is fed via a line 8 as the heating gas to the convectively heated reformer 3, in which it flows around the can from the outside.

The output gas of the reformer 3 is fed via a line 9, in which the heat exchanger 2 and a further heat exchanger 6 are arranged, to a water vapor separator 10, from which the separated water is drawn off via a line 11. The synthesis gas, which now consists of a mixture of carbon monoxide, carbon dioxide and hydrogen and possibly a very small proportion of residual methane, is then fed via line 12 to a carbon dioxide scrubber 13. The washed-out carbon dioxide is returned to

line 1 as a return gas via a line 14 and / or is fed to line 4 and thus to the autothermal reformer 5 via a line 15 led via the heat exchanger 6.

The gas freed from carbon dioxide is fed via line 16 to a hydrogen separator 17; the gas freed from hydrogen is withdrawn as product gas via line 18.

The separated hydrogen can be fed via lines 19 and 20 to the reformers 3 and 5 as recycle gas. The heat exchanger 21 shown in dashed lines in the figure is intended to show that preheating of the recycled hydrogen by the starting gas of the first reforming stage could also be considered if necessary.

Although the end product of the process should be as pure as possible carbon monoxide, gas cleaning stages 10, 13 and 17 are used to set an im essential carbon monoxide-containing product gas with desired proportions of water vapor, carbon dioxide and hydrogen is possible; if necessary, methane can also be fed via a line 22 to the autothermal reformer 5, which is preheated together with the carbon dioxide in the heat exchanger 6.

Due to the direct heating in the autothermal reformer 5 and the convective heating of the reformer 3, no flue gas is generated. The heat supply to the reformer 3 takes place at a high temperature level, and the heat after the reforming stage 3 occurs at low temperatures and can still be integrated into the process by heat exchange with the feed or return gases. The feed gases are fed under pressure so that, with the same pressure drop, the process is carried out with better heat supply and heat transfer conditions.

The cable routings described above are only used to explain the process flow. B. di lines 15 and 22 separate without prior connection into line 4 or can also be performed as separate lines to the reformer 5, or z. B. the line 19 are led directly to the reformer 3 without zuv open into the line 1.

It is only important that the feed gases, starting gases and recycle gases are fed to the individual process stages in order to achieve the inventive goal.

## Claims

1. A process for the production of carbon monoxide, in which a mixture of hydrocarbon, preferably methane, and carbon dioxide in the presence of a catalyst with the supply of heat is fed to at least one reforming stage and carbon dioxide and hydrogen are separated from the reformed starting gas mixture, characterized in that the gas mixture Convectively heated first reforming stage is supplied, the starting gas of the first reforming stage is fed together with oxygen to an autothermal second reforming stage, and the starting gas of the second reforming stage is fed to the convectively heated reforming stage as heating gas.
2. The method of claim 1, thereby characterized that the second reforming step is additionally supplied with carbon dioxide.
3. The method of claim 1 or 2, thereby characterized that the second reforming step is additionally supplied with hydrocarbon.

4. The method according to at least one of claims 1 to 3, characterized in that the separated carbon dioxide is used as the recycle gas.
5. The method according to at least one of claims 1 to 4, thereby characterized that the separated hydrogen is used as a recycle gas.
6. The method according to at least one of claims 1 to 5, so that at least one of the feed gases and/or at least one of the return gases is preheated by heat exchange with the starting gas of the second reforming stage

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                         |                                                 |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------|-------------------------------------------------|
| <b>TRANSMITTAL LETTER TO THE UNITED STATES<br/>DESIGNATED/ELECTED OFFICE (DO/EO/US)<br/>CONCERNING A SUBMISSION UNDER 35 U.S.C. 371</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                         | Attorney Docket No.<br>2110-0010                |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                         | U.S. Application No. (if known, see 37 CFR 1.5) |
| International Application No.<br>PCT/EP2021/054441                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | International Filing Date<br>02/23/2021 | Priority Date Claimed<br>03/06/2020             |
| Title of Invention<br>HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                         |                                                 |
| First Named Inventor<br>Torkild R. Reinertsen                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                         |                                                 |
| <p><b>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.</b></p> <ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> 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.</li> <li>2. <input checked="" type="checkbox"/> 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)).</li> <li>3. An English language translation of the International Application (35 U.S.C. 371(c)(2))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>4. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4))             <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached.</li> <li>b. <input type="checkbox"/> was previously filed in the international phase under PCT Rule 4.17(iv).</li> </ol> </li> </ol> <p><b>Items 5 to 8 below concern amendments made in the international phase.</b></p> <p><u>PCT Article 19 and 34 amendments</u></p> <ol style="list-style-type: none"> <li>5. <input type="checkbox"/> 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)).</li> <li>6. <input type="checkbox"/> English translation of the PCT Article 19 amendment is attached (35 U.S.C. 371(c)(3)).</li> <li>7. <input type="checkbox"/> 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)).</li> </ol> <p><u>Cancellation of amendments made in the international phase</u></p> <ol style="list-style-type: none"> <li>8a. <input type="checkbox"/> Do not enter the amendment made in the international phase under PCT Article 19.</li> <li>8b. <input type="checkbox"/> Do not enter the amendment made in the international phase under PCT Article 34.</li> </ol> <p>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).</p> <p><b>The following items 9 to 17 concern a document(s) or information included.</b></p> <ol style="list-style-type: none"> <li>9. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>10. <input checked="" type="checkbox"/> A preliminary amendment.</li> <li>11. <input checked="" type="checkbox"/> An Application Data Sheet under 37 CFR 1.76.</li> <li>12. <input type="checkbox"/> A substitute specification. NOTE: A substitute specification cannot include claims. See 37 CFR 1.125(b).</li> <li>13. <input checked="" type="checkbox"/> A power of attorney and/or change of address letter.</li> <li>14. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.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).</li> <li>15. <input type="checkbox"/> Assignment papers (cover sheet and document(s)). Name of Assignee: _____</li> <li>16. <input type="checkbox"/> 37 CFR 3.73(c) Statement (when there is an Assignee).</li> </ol> |                                         |                                                 |

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.

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|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                                                                               |         |                                         |                     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|-------------------------------------------------------------------------------|---------|-----------------------------------------|---------------------|
| U.S. APPLN. No. (if known – see 37 CFR 1.5)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |              | INTERNATIONAL APPLICATION No.<br><b>PCT/EP2021/054441</b>                     |         | ATTORNEY DOCKET No.<br><b>2110-0010</b> |                     |
| 17. <input type="checkbox"/> Other items or information:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |              |                                                                               |         |                                         |                     |
| <b>The following fees have been submitted.</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |              |                                                                               |         |                                         | <b>CALCULATIONS</b> |
| 18. <input checked="" type="checkbox"/> Basic national fee (37 CFR 1.492(a)) ..... \$320                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |              |                                                                               |         |                                         | \$ 320              |
| 19. <input checked="" type="checkbox"/> Examination fee (37 CFR 1.492(c))                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |              |                                                                               |         |                                         | \$ 800              |
| <ul style="list-style-type: none"> <li>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</li> <li>All other situations ..... \$800</li> </ul>                                                                                                                                                                                                                                                                                                                         |              |                                                                               |         |                                         |                     |
| 20. <input checked="" type="checkbox"/> Search fee (37 CFR 1.492(b))                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |              |                                                                               |         |                                         | \$ 540              |
| <ul style="list-style-type: none"> <li>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</li> <li>Search fee (37 CFR 1.445(a)(2)) has been paid on the international application to the USPTO as an International Searching Authority ..... \$140</li> <li>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..... \$540</li> <li>All other situations ..... \$700</li> </ul> |              |                                                                               |         |                                         |                     |
| <b>TOTAL OF 18, 19, and 20 =</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |              |                                                                               |         |                                         | <b>\$ 1660</b>      |
| <input type="checkbox"/> 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 ..... \$420                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |              |                                                                               |         |                                         |                     |
| Total Sheets                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Extra Sheets | Number of each additional 50 or fraction thereof (round up to a whole number) |         | RATE                                    |                     |
| - 100 =                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | / 50 =       |                                                                               |         | x \$420                                 |                     |
| 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))..... \$160                                                                                                                                                                                                                                                                                                                                                                                                                                   |              |                                                                               |         |                                         | \$                  |
| CLAIMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | NUMBER FILED | NUMBER EXTRA                                                                  | RATE    |                                         |                     |
| Total claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 20 - 20 =    | 0                                                                             | x \$100 |                                         | \$                  |
| Independent claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 3 - 3 =      | 0                                                                             | x \$480 |                                         | \$                  |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |              |                                                                               | + \$860 |                                         | \$                  |
| Fee for submission of Sequence Listing text file of 300 MB to 800 MB (37 CFR 1.21(o)(1))..... \$1,060                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |              |                                                                               |         |                                         | \$                  |
| Fee for submission of Sequence Listing text file of more than 800 MB (37 CFR 1.21(o)(2))..... \$10,500                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |              |                                                                               |         |                                         | \$                  |
| Processing fee for furnishing the English translation later than 30 months from the earliest claimed priority date (37 CFR 1.492(i))..... \$140 +                                                                                                                                                                                                                                                                                                                                                                                                                                                               |              |                                                                               |         |                                         | \$                  |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |              |                                                                               |         |                                         | <b>\$ 1660</b>      |
| <input type="checkbox"/> Applicant asserts small entity status. See 37 CFR 1.27. Fees above are reduced by 1/3.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |              |                                                                               |         |                                         |                     |
| <input type="checkbox"/> Applicant certifies micro entity status. See 37 CFR 1.29. Fees above are reduced by 3/4. Applicant must attach form PTO/SB/15A or B or equivalent.                                                                                                                                                                                                                                                                                                                                                                                                                                     |              |                                                                               |         |                                         |                     |
| <b>TOTAL NATIONAL FEE =</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |              |                                                                               |         |                                         | <b>\$ 1660</b>      |
| 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 +                                                                                                                                                                                                                                                                                                                                                                                                                                    |              |                                                                               |         |                                         | \$                  |
| <b>TOTAL FEES ENCLOSED =</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |              |                                                                               |         |                                         | <b>\$ 1660</b>      |

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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. 501039 in the amount of \$ 1660 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. 501039 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).
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**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: 26568 OR ☐ Correspondence address below

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|-------------------|------------------|-----------------------------------|-------------------|
| Signature         | /Paul C. Craane/ | Date                              | September 1, 2022 |
| Name (Print/Type) | Paul C. Craane   | Registration No. (Attorney/Agent) | 38,851            |

## 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.

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
16 July 2009 (16.07.2009)

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(10) International Publication Number  
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61/009,983 4 January 2008 (04.01.2008) US

(71) Applicant (for all designated States except US): **TRIB-UTE CREATIONS, LLC** [US/US]; 49 High Street, Farmington, CT 06032 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **FEINSTEIN, Jonathan, Jay** [US/US]; 9A Crosby Road, North Salem, NY 10560 (US). **RALSTON, Michael, P.** [US/US]; 12231 South 18th East Avenue, Jenks, OK 74037 (US).

(74) Agent: **MICHAL, Robert, P.**; Frishauf, Holtz, Goodman & Chick, P.C., 220 Fifth Avenue, New York, New York 10001-7708 (US).

(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, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(54) Title: STEAM REFORMING WITH SEPARATION OF PSA TAIL GASES

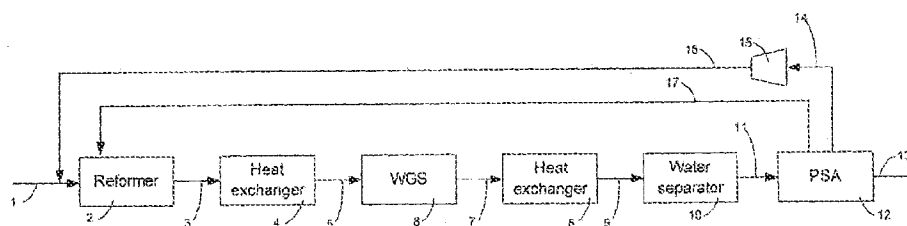


Figure 1

(57) Abstract: Steam and a hydrocarbon feedstock are reformed in a combustion heated reformer in a manner in which the energy content of the PSA tail gas downstream exceeds the heating requirements of the reformer. The syngas is separated in one or more PSA units into at least a high purity hydrogen stream, at least one process gas recycle stream containing tail gas energy units exceeding the energy units required for heating the reformer, and a burner stream containing the balance of the PSA inlet gases and preferably containing no more energy units than are required for heating the reformer. The recycle streams are recycled as process gas to the reformer, the PSA or both, and the burner stream is used for heating the reformer.

WO 2009/088971 A1



## STEAM REFORMING WITH SEPARATION OF PSA TAIL GASES

### Cross-Reference to Related Application

This application claims the benefit under 35 USC 119 of U.S. Provisional Patent Application Serial No. 61/009,983 filed January 4, 2008, the entire disclosure of which is incorporated herein by reference.

### Field of Invention

The present invention relates generally to the field of gas separation.

### Background Information

A "PSA unit" as used herein shall mean a pressure swing adsorption bed or group of beds working in parallel such that high and low pressure effluent flows from each of the parallel beds in the PSA unit to the next process unit or use point. Process gases may flow symmetrically back and fourth between multiple beds of a PSA unit without exiting the PSA unit. Multiple PSA units or the like shall describe the use of more than one bed or groups of beds such that a given high or low pressure effluent stream from one bed or group of beds subsequently passes unilaterally to a second bed or group of beds.

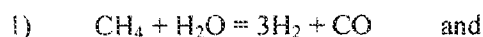
All references to percentages of gas content herein refer to volume percentages.

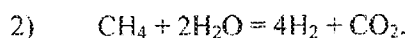
A steam-to-carbon ratio or S/C ratio is defined herein as the ratio of water molecules in the steam to the carbon atoms in the hydrocarbon feedstock of the steam and hydrocarbon mixture that are reformed in a reformer.

Unrecovered H<sub>2</sub> is defined herein as all H<sub>2</sub> exiting a PSA unit not contained in the product or high purity H<sub>2</sub> stream.

High purity H<sub>2</sub> is defined herein as gas containing at least 90% H<sub>2</sub> and preferably at least 99% H<sub>2</sub>.

Steam methane reforming (SMR) processes are used to produce hydrogen, or a mixture of at least H<sub>2</sub> and CO, referred to herein as syngas, by combining steam and a hydrocarbon such as methane at temperatures of up to about 860° C and pressures generally in excess of 10 bar to form hydrogen and syngas according to the reactions

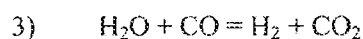




Although no more than 2 moles of steam per mole of carbon (S/C) in the hydrocarbon are required stoichiometrically, S/C ratios in excess of stoichiometric steam requirements are typically used in this process, consuming additional energy to generate steam. Energy cannot be recovered effectively from the unreacted steam because the steam exits the reformer in dilute form mixed with other gas species, substantially lowering the temperature at which it condenses to a temperature below the range for useful heat sources for the SMR process. It would be desirable to operate the SMR process at a lower S/C ratio in such a way that the energy to generate steam could be economically reduced.

Conventional SMR operation is typically at S/C ratios of about 2.2 to 1 or higher because of limitations of the reforming catalyst. At high heat fluxes into the reforming tubes and at lower S/C ratios the catalyst tends to form coke, fouling the process. The use of new catalytic reactor designs, however, makes it possible to operate the reformer at S/C ratios of less than 2.8 to 1 without coking. This in turn creates a new need for a way of utilizing significantly higher PSA tail gas energy content so that the energy savings associated with reducing the amount of steam supplied to the reforming process can be monetized.

At lower ratios of S/C the amount of unreacted steam, referred to herein as steam slip, in the gas exiting the reformer decreases, but the amount of unreacted methane, referred to herein as methane slip, increases. Gases exiting the reformer are typically cooled and passed through a water gas shift reactor to further promote the reaction



at temperatures of 200° to 400° C. A large portion of the unreacted steam is then removed by cooling the syngas and passing it through a liquid phase water separator. The resulting syngas is often next separated by a PSA unit into a high purity hydrogen stream and a tail gas stream of the remaining species of CO<sub>2</sub>, CH<sub>4</sub>, CO, unrecovered H<sub>2</sub>, some H<sub>2</sub>O, and contaminants such as N<sub>2</sub> or Ar.

Tail gas containing a limited amount of methane slip can be utilized as fuel for the burners in the reformer. SMR operation at S/C ratios of less than 2.8, referred to herein as steam lean reforming, causes greater methane slip to exit the reformer and water gas shift reactor than at higher S/C ratios in which the methane slip can be fully utilized as a fuel for

the burners in the reformer. At S/C ratios less than about 2.8 to 1 and particularly below 2 to 1, the increased methane slip causes the combustion energy content of the tail gas to exceed the heating requirements of the burners in the reformer.

Other methods, collectively referred to herein as parallel reforming, consist of a first stream of a hydrocarbon and steam being heated and reformed in a combustion heated first reformer and a second stream of a hydrocarbon and steam being heated and reformed with heat from the outlet reformed gas or from the flue gas from the first reformer. Because parallel reforming reforms more hydrocarbon and steam for a given amount of combustion heat compared to practices in which all of the hydrocarbon and steam are heated and reformed in a combustion heated reformer, the energy content of the resulting downstream PSA tail gas for parallel reforming is increased and may be in excess of the heat required by the combustion heated reformer.

The gas energy content of the PSA tail gas downstream of parallel reforming or steam lean reforming which is in excess of the combustion heated reformer requirements could be used to generate steam export from the SMR plant, but in many situations the steam may not be needed. If used in a gas turbine for driving compressors, the excess energy units may or may not be competitive to the alternative use of an electric motor. Further, the tail gas may contain sufficient quantities of CO, CO<sub>2</sub>, and/or H<sub>2</sub> as to prohibit its use as an export fuel, gas turbine fuel or in other applications. It may therefore be necessary to consume all of the tail gas energy within the SMR plant to monetize the energy savings that result from lowering the amount of fuel needed for combustion heating of the reformer in lean steam or parallel reforming practices.

Wet scrubbing by physical or chemical absorption of CO<sub>2</sub> into an amine or carbonate solution to extract CO<sub>2</sub> from syngas is known. Use of wet scrubbing in combination with PSA is known to enable co-production of H<sub>2</sub> and CO<sub>2</sub>.

US Patent 5,669,960, incorporated herein by reference in its entirety, teaches the use of a single PSA unit to separate syngas from an SMR reformer and water gas shift unit into a high purity hydrogen stream, a combustible-rich tail gas stream, and a third stream that is combustible-lean and carbon dioxide-rich. The purpose is to concentrate the energy content of the tail gas into a smaller volume of gas. This in turn permits the use of this tail gas as a burner fuel which produces a stable flame or as a recycled feedstock to the

reformer. With regard to using the tail gas as fuel for the burners in the reformer, the prior art solves a problem related to conventional SMR reforming in which the tail gas may have insufficient combustion energy content to support a stable flame. It does not anticipate the existence of a PSA tail gas that has energy concentration suitable for stable flames and energy content in excess of that required for burner fuel, its need for treatment, or a method for its treatment. With regard to using the combustible-rich stream as recycled feedstock to the reformer, known techniques do provide a method for expelling carbon units, but is significantly ineffective in providing feedstock for further reforming reaction. As taught, the combustible-rich stream contains  $\text{CH}_4$  and the unrecovered  $\text{H}_2$  in the PSA unit. Because reforming reactions 1 and 2 are thermodynamically reversed in accordance with the third and fourth powers of the  $\text{H}_2$  partial pressure, respectively, use of gas containing the proportions of  $\text{H}_2$  taught or implied in the prior art is relatively ineffective for the promotion of reactions 1 and 2 in the forward direction. The  $\text{H}_2$  units recycled to the reformer along with the recycled  $\text{CH}_4$  would prevent the  $\text{CH}_4$  from effectively reacting, while burdening the reformer with additional pressure drop and heating requirements. To separate the  $\text{CH}_4$  from the unrecovered  $\text{H}_2$  requires methods not disclosed or implied in prior art, for the purpose of reacting the recycled  $\text{CH}_4$  more completely. Neither the concept nor the advantage of recirculating  $\text{CH}_4$  to the feed gas stream to the reformer while selectively preventing the recirculation of product  $\text{H}_2$  to the reformer of a plant producing and recovering  $\text{H}_2$  are disclosed, taught or suggested in prior art.

US Patent 6,500,241, incorporated herein by reference in its entirety, teaches co-production of  $\text{H}_2$  and  $\text{CO}_2$  from syngas evolved from a reformer or partial oxidation unit followed by a water gas shift reactor. In one embodiment taught in US Patent 6,500,241 (see column 3, lines 19-42 thereof) a wet scrubbing unit is used in combination with a  $\text{H}_2$  PSA unit and a liquefaction unit. In another embodiment (see column 5, lines 39-51 thereof) the patent teaches the use of a  $\text{CO}_2$  PSA unit, a  $\text{H}_2$  PSA unit, and a liquefaction unit. The recycling of an intermediate stream to the  $\text{H}_2$  PSA for increased  $\text{H}_2$  yield is taught. Use of either of the disclosed combinations of three separation process units requires substantially more capital equipment investment.

#### Summary of the Invention

It is an object of the present invention to provide a SMR process wherein the fuel requirements for reforming are less than the energy content of the downstream PSA tail gas

and wherein the energy contained in the PSA tail gas is effectively and economically utilized.

It is another object of the present invention to produce more hydrogen product from a given molar volume of steam and methane reactants entering an SMR reactor.

It is still another object of the present invention to reduce the amount of separation equipment used to separate CO<sub>2</sub> for export into a useful product, or for sequestration from the atmosphere.

It is yet a further object of the present claimed invention to reduce the thermal mass of flue gas from the reformer.

Other benefits will become apparent from the disclosure to one of ordinary skill in the art.

Steam and a hydrocarbon feedstock are reformed in a combustion heated reformer in such a way that the fuel requirements for reforming are less than the energy content of the downstream PSA tail gas, preferably by employing at least one of reformer at a S/C ratio of less than 2.8 and more preferably less than 2 to 1 or by employing parallel reforming. The syngas is separated in one or more PSA units into at least a stream containing high purity hydrogen, at least one process gas recycle stream containing tail gas energy units which together with the burner stream exceed the energy units required for heating the reformer, and a burner stream containing the balance of the PSA inlet gases and preferably containing no more energy units than are required for heating the reformer. The recycle streams are recycled as process gas to the reformer, the PSA, or both, and the burner stream is used for heating the reformer.

#### **Brief Description of Drawings**

FIG. 1 is a schematic representation of the present invention according to a first embodiment.

FIG. 2 is a schematic representation of the present invention according to a second embodiment.

FIG. 3 is a schematic representation of the present invention according to a third embodiment.

FIG. 4 is a schematic representation of the present invention according to a preferred fourth embodiment.

FIG. 5 is a schematic representation of the present invention according to a fifth embodiment.

FIG. 6 is a schematic representation of the present invention according to a sixth embodiment.

### **Detailed Description**

The following detailed description discloses various exemplary embodiments and features of the invention. These exemplary embodiments and features are not meant to be limiting of the claimed invention.

Referring now to Figure 1, a hydrocarbon feedstock such as methane is combined with steam at a S/C ratio of less than 2.8 and preferably less than 2, or steam and a hydrocarbon are parallel reformed. Reforming preferably takes place at a pressure in excess of 10 bar and the mixture is introduced together via line 1 into one or more reformers 2 wherein the reactants are heated and reacted to form a syngas in the presence of a suitable catalyst. While one reformer 2 is shown in Fig. 1, it is foreseen that more than one reformer may be employed. Use of a reforming catalytic reactor with high effective catalyst loading and high axial heat transfer enables reforming to take place at low S/C ratios without forming coke deposits in the reforming catalytic reactor. US patent application 2006/0008399A1 and WIPO patent application WO2006/058060A2, which are incorporated herein by reference in their entirety, teach examples of suitable reforming catalytic reactors.

The outlet syngas from the reformers is conveyed by line 3 to heat exchanger 4 in which the syngas is cooled to a temperature of around 200°C. The syngas is preferably conveyed by line 5 to optional water gas shift reactor 6 in which the H<sub>2</sub>O and CO contents of the syngas are reduced and the H<sub>2</sub> and CO<sub>2</sub> contents are increased. The syngas is

preferably conveyed by line 7 to optional heat exchanger 8 in which the syngas is further cooled. The syngas is preferably then conveyed by line 9 to optional water separation unit 10 in which water condensate is removed.

The partially dried syngas is then conveyed by line 11 to a PSA unit 12 in which the syngas is separated into various product and tail gas streams. The PSA unit is a conventional  $H_2$  PSA unit as is typically used in an SMR plant. The PSA unit is fitted with valves to separate the inlet gas, which is provided to the PSA unit, into a high purity  $H_2$  stream designated the product stream, and two tail gas streams designated the burner stream and the feedstock stream, respectively. The product stream containing high purity  $H_2$  exits the PSA unit via line 13. A feedstock stream exits the PSA unit via line 14, is subsequently compressed in compressor 15, and is recycled to the process gas inlet line 1 of the reformer via line 16. A burner stream exits the PSA unit via line 17, which conveys the burner stream to the reformer burners (not shown) providing at least part of the burner fuel requirements. Line 17 may contain a blower or compressor (not shown).

The product stream provided in line 13 contains most of the inlet  $H_2$  to the PSA unit in the form of high purity  $H_2$ . The product stream exits the product or high pressure outlet end of each bed in the PSA unit. The feedstock stream contains  $CH_4$ , most of the  $H_2O$  and  $CO_2$ , and some of the unrecovered hydrogen. The feedstock stream preferably contains at least all tail gas energy units in excess of the energy units required for the reformer burner fuel requirements, with as much of those excess energy units as possible being in the form of  $CH_4$  and as few as possible being in the form of  $H_2$ . The burner stream contains the balance of the inlet gas to the PSA unit and preferably contains no more energy units than are required for heating the reformer. All tail gas streams of each embodiment exit the opposite end of each bed from the product stream. The method and apparatus for separating the tail gas into multiple streams of different compositions from each other are described below.

Referring now to Fig. 2, a second embodiment is illustrated in which all components corresponding to Figure 1 have the same numbering as in Fig. 1. In the second embodiment all of the components of the first embodiment are employed, and an additional tail gas stream designated the  $CO_2$  stream is conveyed from PSA unit 12 via line 18. In the second embodiment the  $CO_2$  stream contains most of the  $H_2O$  and  $CO_2$  from the inlet gas to the PSA unit. The product stream contains high purity hydrogen, and the feedstock stream

contains at least some of the energy units exceeding the energy units required for heating the reformer. The burner stream contains the balance of the inlet gas to the PSA unit, including most of the unrecovered  $H_2$  and preferably contains no more energy units than are required for heating the reformer. The  $CO_2$  stream is vented, beneficiated into a useful product, or sequestered from the atmosphere.  $CO_2$  beneficiation may be by means of compression, further purification, or both.

Referring now to Fig. 3, a third embodiment is illustrated in which all components corresponding to Fig. 1 have the same numbering as in Fig. 1. In the third embodiment all of the components of the first embodiment are employed, and an additional tail gas stream designated the PSA recycle stream is conveyed from PSA unit 12 via line 19, which is compressed in compressor 20 and is then returned via line 21 to the inlet line of PSA unit 12 or is equivalently returned to PSA unit 12. In the third embodiment the product and feedstock stream gas contents are as defined above in connection with the first embodiment. The PSA recycle stream contains a substantial portion of the unrecovered  $H_2$ . As progressively higher portions of the unrecovered  $H_2$  are included in the PSA recycle stream, they will be increasingly mixed with  $CO$ ,  $CH_4$  and other tail gas components and the concentration of  $H_2$  in the PSA recycle stream will decline. The PSA recycle stream preferably contains only as much  $H_2$  as is possible consistent with a suitable  $H_2$  concentration so as to make its compression and recovery via PSA unit 12 economically attractive in view of its effect on net capital and energy costs. The burner stream contains the balance of the inlet gas to PSA unit 12 and preferably contains no more energy units than are required for heating the reformer.

Referring now to Fig. 4, a preferred fourth embodiment is illustrated in which all components corresponding to Fig. 3 have the same numbering as in Fig. 3. In the fourth embodiment all of the components of the third embodiment are employed, and an additional tail gas stream designated the  $CO_2$  stream is conveyed from PSA unit 12 via line 18. In the fourth embodiment the product and PSA recycle stream gas contents are as defined in the third embodiment, the feedstock stream contains at least some of the energy units in excess of the energy requirements for heating the reformer, the  $CO_2$  stream contains most of the  $H_2O$  and  $CO_2$  from the inlet gas to the PSA unit, and the burner stream contains the balance of the inlet gas to the PSA unit and preferably contains no more energy units than are required for heating the reformer.



Referring now to Fig. 5, a fifth embodiment is illustrated in which all components corresponding to Fig. 1 have the same numbering as in Fig. 1. In the fifth embodiment all of the components of the first embodiment are employed except that items 14, 15, and 16 for conveying a feedstock stream to the reformer inlet line are not included, and an additional tail gas stream designated the PSA recycle stream is conveyed from PSA unit 12 via line 19, is compressed in compressor 20 and returned via line 21 to PSA inlet line 11 or is equivalently returned to PSA unit 12. In the fifth embodiment the product stream gas content is high purity  $H_2$ . The PSA recycle stream contains a substantial portion of the unrecovered  $H_2$ . As progressively higher portions of the unrecovered  $H_2$  are included with the PSA recycle stream, they will be increasingly mixed with  $CO$ ,  $CH_4$  and other tail gas components and the concentration of  $H_2$  in the PSA recycle stream will decline. The PSA recycle stream preferably contains only as much  $H_2$  as is possible consistent with a suitable  $H_2$  concentration so as to make its compression and recovery via the PSA unit economically attractive in view of its effect on net capital and energy costs. The burner stream contains the balance of the inlet gas to the PSA unit and preferably contains no more energy units than are required for heating the reformer. No tail gas is separated or recirculated as feedstock to the reformer inlet. In this embodiment the energy units in excess of those required for use in the reformer burners is separated from the tail gas in the form of  $H_2$  for recirculation to the PSA unit, as opposed to in all other embodiments in which the excess energy units are at least partly separated in the form of  $CH_4$  for recirculation to the reformer.

The tail gas streams are separated from each other as required in each embodiment by timing the opening and closing of valves at the tail gas outlet end of each PSA bed to allow the gas exiting each bed at particular times to be directed to the respective tail gas outlet lines described in the respective embodiments. While not being held to this explanation or sequence, it is understood that molecular sieves used in PSA units for separating a high purity  $H_2$  product have different adsorptive affinities for  $H_2O$ ,  $CO_2$ ,  $CH_4$ ,  $CO$ , and  $H_2$ , such that these respective gases exit PSA beds as tail gas in this approximate and overlapping sequence during the collective depressurization and purge portions of a complete PSA process cycle. Where such molecular sieves are used, the  $CO_2$  stream, followed by the feedstock stream followed by the burner stream followed by the PSA recycle stream are diverted from a given bed by opening only valves to lines 18, 17, 14, and 19, respectively, while all other valves to outlet lines are closed, to the extent that each of

these respective tail gas streams is employed in the respective embodiments. Any or all outlet lines 18, 17, 14, and 19, respectively, may contain a surge tank. If more than one type of molecular sieve is used in a bed, the various molecular sieves are preferably layered from the gas inlet end to the H<sub>2</sub> product outlet end in such sequence as to accentuate H<sub>2</sub> recovery and separation of the tail gas stream compositions from each other. If multiple PSA units are used, different molecular sieves are preferably used in the sequence of PSA units as to accentuate H<sub>2</sub> recovery and separation of the tail gas stream compositions from each other.

Referring now to Fig. 6, a sixth embodiment is illustrated in which all components corresponding to Fig. 3 have the same numbering as in Fig. 3. In the sixth embodiment syngas is conveyed from water separator 10 via line 22 to PSA unit 23, in which the syngas is separated into a first stream and a CO<sub>2</sub> stream. The first stream is conveyed via line 11 to PSA unit 12, which corresponds to PSA unit 12 in Figure 3. All outlet lines from PSA unit 12 correspond to those of like numbering exiting unit 12 in Figure 3. The CO<sub>2</sub> stream is exported from PSA unit 23 and from the system via line 24. PSA unit 23 contains a molecular sieve for separating H<sub>2</sub>O and CO<sub>2</sub> from syngas. The CO<sub>2</sub> stream exported via line 24 contains most of the H<sub>2</sub>O and CO<sub>2</sub> entering PSA unit 23, and preferably contains less than 10% CH<sub>4</sub> and yet smaller volume percentages of CO and H<sub>2</sub>. The balance of the syngas entering PSA unit 23 is conveyed to PSA unit 12 via line 11. A PSA recycle stream exits PSA unit 12 via line 19 and preferably contains only as much H<sub>2</sub> as is possible consistent with a suitable H<sub>2</sub> concentration so as to make its compression and recovery via PSA unit 12 economically attractive in view of its effect on net capital and energy costs. A feedstock stream exits PSA unit 12 via line 14 and contains at least some of the energy units exceeding the energy requirements needed for heating the reformer. A burner stream exits PSA unit 12 via line 14 and contains the balance of the inlet gas to PSA unit 12. The burner stream preferably contains no more energy units than are required for heating in the reformer.

It is foreseen that other embodiments to separate the syngas into the equivalent of product, burner, and process gas recycle streams as taught in any of the preceding embodiments via the combination of multiple PSA units can be devised by a person of ordinary skill in the art to which the present invention pertains.

Although the present invention has been described in terms of certain preferred embodiments, various features of separate embodiments can be combined to form additional embodiments not expressly described. Moreover, other embodiments apparent to those of ordinary skill in the art after reading this disclosure are also within the scope of this invention. Furthermore, not all of the features, aspects and advantages are necessarily required to practice the present invention. Thus, while the above detailed description has shown, described, and pointed out novel features of the invention as applied to various embodiments, it will be understood that various omissions, substitutions, and changes in the form and details of the apparatus or process illustrated may be made by those of ordinary skill in the art without departing from the scope and spirit of the invention. The invention may be embodied in other specific forms not explicitly described herein. The embodiments described above are to be considered in all respects as illustrative only and not restrictive in any manner. Thus, scope of the invention is indicated by the following claims rather than by the foregoing description.

We claim:

1. A steam reforming process comprising:  
reforming steam and a hydrocarbon feedstock to form syngas in a combustion-heated reformer;  
separating the syngas in at least one PSA unit into at least a high purity hydrogen stream, a feedstock stream containing  $\text{CH}_4$  constituting at least some of energy units in excess of those required for combustion in the reformer, and a burner stream containing the balance of the inlet gas to the at least one PSA unit, including unrecovered  $\text{H}_2$ , and  
recycling at least a portion of the burner stream to the combustion-treated reformer for combustion therein, and  
recycling at least a portion of the feedstock stream to a reformer feedstock inlet.
2. The steam reforming process according to claim 1 wherein the separation of syngas into feedstock and burner streams comprises venting purge gases from respective beds of the at least one PSA unit at different times within respective purge cycles to respective feedstock and burner streams.
3. The steam reforming process according to claim 1 wherein the separation of tail gases into feedstock and burner streams comprises utilizing multiple PSA units in which purge gas from a first PSA unit is vented to the feedstock stream and purge gas from a second PSA is vented to the burner stream.
4. The steam reforming process according to claim 1 wherein the tail gases are separated into at least one of a PSA recycle stream which is recycled to at least one PSA unit or a carbon dioxide rich outlet stream.
5. A steam reforming process comprising:  
reforming steam and a hydrocarbon to form syngas in a combustion-heated reformer;  
separating the syngas in at least one PSA unit into at least a high purity hydrogen stream, a PSA recycle stream containing some of the recovered  $\text{H}_2$  constituting at least

some of the energy units in excess of those required for combustion in the combustion-treated reformer, and a burner stream containing the balance of the inlet gas to the at least one PSA unit,

compressing and recycling at least a portion of the PSA recycle stream to the at least one PSA unit, and

recycling at least a portion of the burner stream to the combustion-treated reformer for combustion therein.

6. The steam reforming process according to claim 5 wherein the separation of tail gases into PSA recycle and burner streams comprises venting purge gases from respective beds of the at least one PSA unit at different times within respective purge cycles to respective PSA recycle and burner streams.

7. The steam reforming process according to claim 5 wherein the separation of tail gases into PSA recycle and burner streams comprises utilizing a plurality of multiple PSA units in which purge gas from a first PSA unit is vented to the burner stream and purge gas from a second PSA of the first PSA is vented to a PSA recycle stream.

8. The steam reforming process according to claim 5 wherein the tail gases are separated into at least one of a feedstock stream which is recycled to the reformer feedstock inlet or a carbon dioxide rich outlet stream.

9. A steam reforming apparatus comprising:

a combustion heated reformer for reforming steam and a hydrocarbon feedstock to form syngas, the combustion heated reformer having an inlet and an outlet;

at least one PSA unit operatively coupled to the combustion heated reformer to separate the syngas into at least a high purity hydrogen stream, a fuel stream for combustion heating in the combustion heated reformer and a process recycle stream, the at least one PSA unit having an inlet and a plurality of outlets, the fuel stream being provided from the at least one PSA to the combustion heated reformer for combustion heating;

means for conveying the high purity hydrogen stream from a respective one of the plurality of outlets of the at least one PSA unit; and

means for recycling the process recycle stream from a respective one of the plurality of outlets of the at least one PSA unit to at least one of the inlet of combustion heated reformer or the inlet of the at least one PSA unit.

10. The stream reforming apparatus according to claim 9, wherein the process recycle stream contains at least some of energy units of the fuel stream and process recycle stream in excess of those required for combustion in the combustion heated reformer, and the fuel stream contains a remainder of the inlet gas to the at least one PSA unit not distributed to the high purity hydrogen stream or to the process recycle stream.

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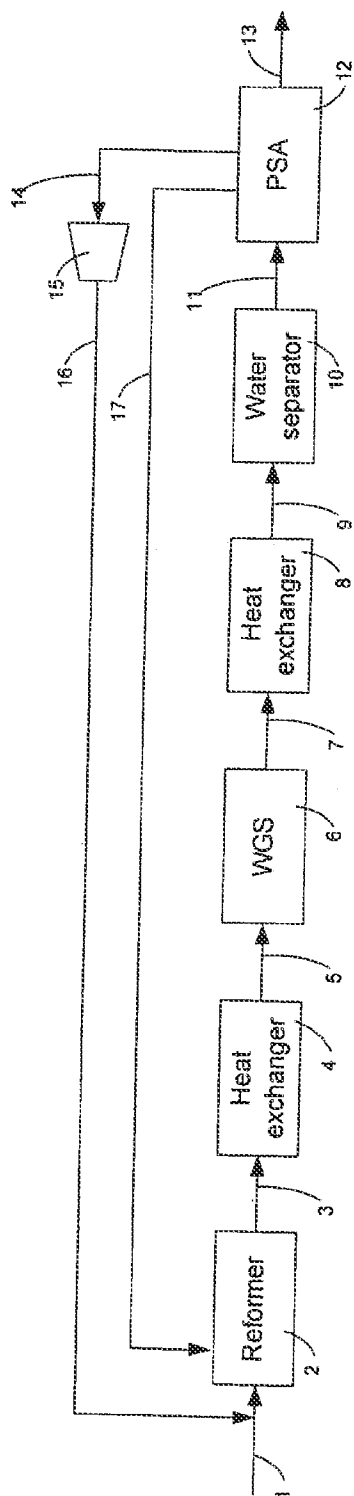


Figure 1

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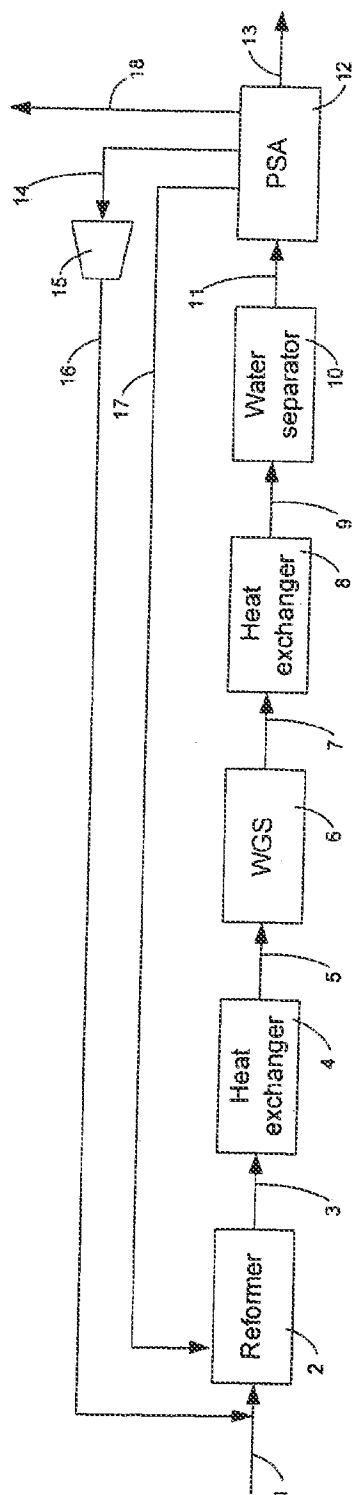


Figure 2



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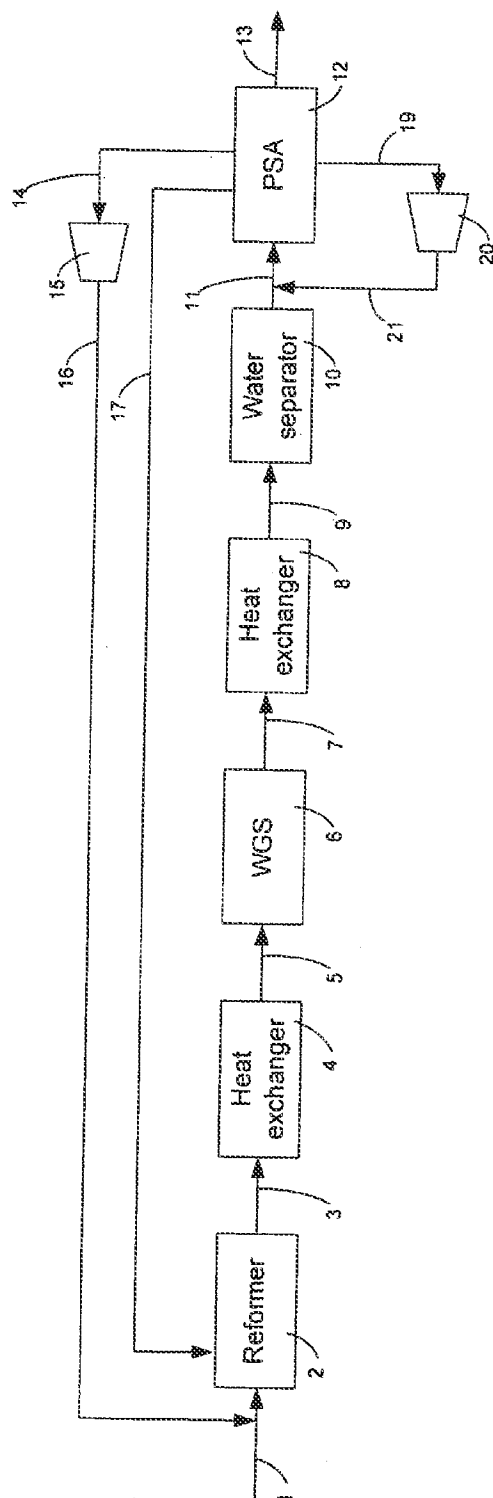


Figure 3

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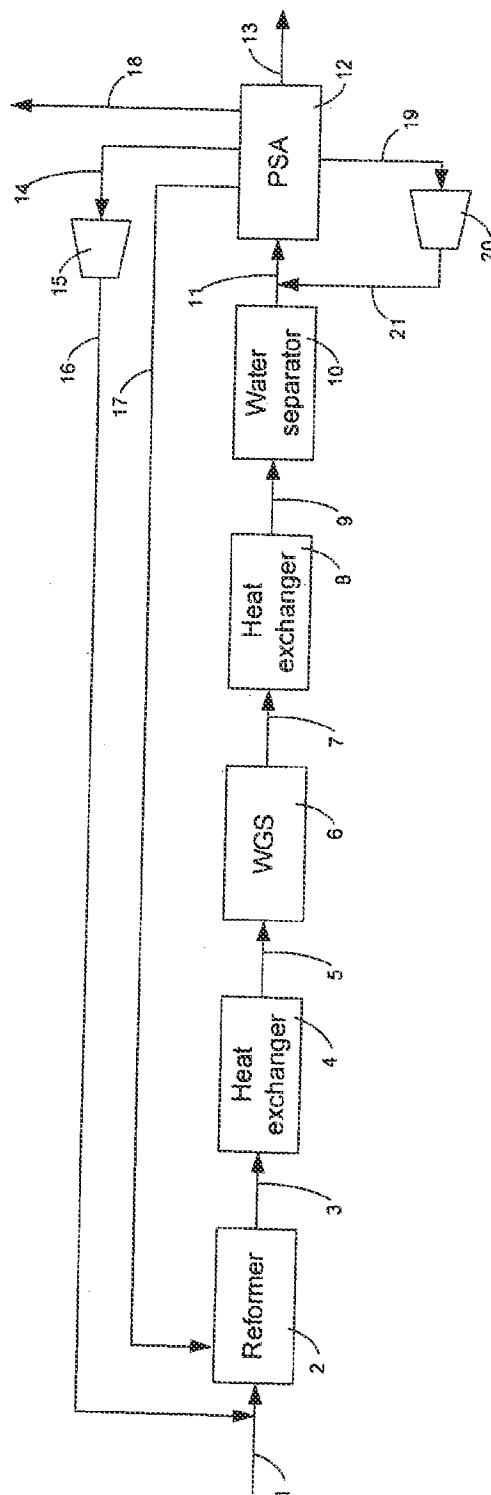


Figure 4

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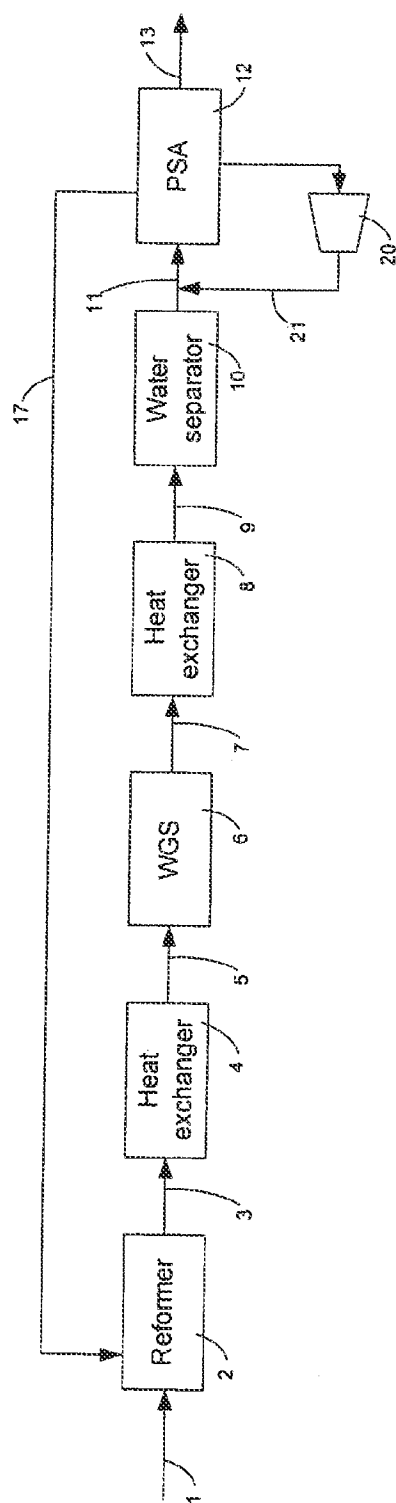


Figure 5

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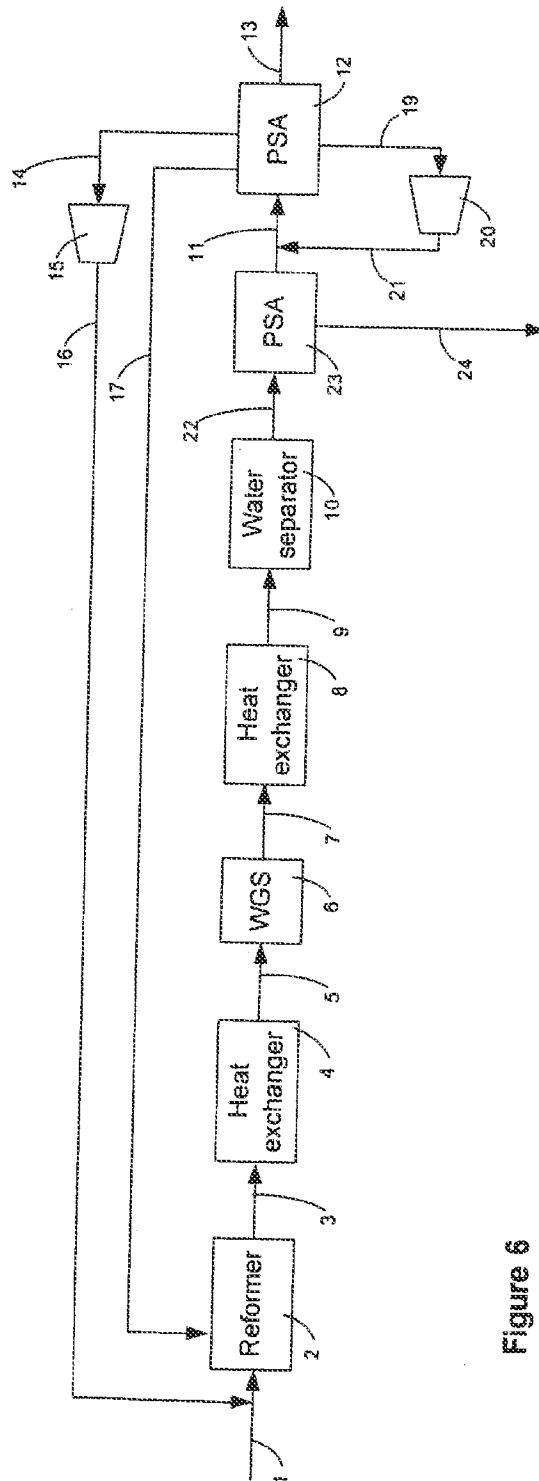


Figure 6

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/00022

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 53/02 (2009.01)

USPC - 96/134

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC (8) - B01D 53/02 (2009.01)

USPC - 96/134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PUBWEST (PGPB,USPT,USOC,EPAB,JPAB) Terms - tail waste offgas PSA burner combustor furnace heater steam reforming  
compress swing adsorption Tribute

Google - steam reformer recycle PSA tail gases; reformer recycle PSA tail gas BTU; compress PSA stream burner

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                      | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | US 2007/0264186 A1 (DYBKJAER, ET AL.) 15 November 2007 (05.11.2007), paras [0011]-[0014], [0036]-[0037] | 1-10                  |
| Y         | US 2005/0066813 A1 (DUNN) 31 March 2005 (31.03.2005), para [0014]                                       | 1-4                   |
| Y         | US 2006/0156921 A1 (MONEREAU, ET AL.) 20 July 2006 (20.07.2006), para [0006], [0014]                    | 5-10                  |
| Y         | US 6,183,626 B1 (BAKER, ET AL.) 06 February 2001 (06.02.2001), col 7, ln 54-63                          | 2, 6                  |

☐ Further documents are listed in the continuation of Box C.

## \* Special categories of cited documents:

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

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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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 February 2009 (13.02.2009)

Date of mailing of the international search report

23 FEB 2009

Name and mailing address of the ISA/US

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PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. Not yet assigned                      Confirmation No. Not yet assigned

Inventor(s): Torkild R. Reinertsen et al.

Filed: February 23, 2021

Art Unit: Not yet assigned

Examiner: Not yet assigned

Attorney's Docket No. 2110-0010

Customer No. 26568

Title: Hydrogen and/or Ammonia Production Process

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

**PRELIMINARY AMENDMENT**

Sir:

Prior to action on the merits, please amend the above-identified application as follows:

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

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

**Remarks/Arguments** begin on page 10 of this paper.

Application No. Not yet assigned  
Preliminary Amendment Dated September 1, 2022

**Amendments to the Specification:**

Please insert the following amended paragraph before page 1, line 1:

The present application is a U.S. National Stage of PCT International Patent Application No. PCT/EP2021/054441, filed February 23, 2021, which claims priority to GB Application Nos. 2003317.1, filed March 6, 2020, and 2010174.7, filed July 2, 2020, both of which are hereby incorporated herein by reference.

**Amendments to the Claims:**

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

**Listing of Claims:**

1 (previously presented). A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and

the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.



2 (currently amended). The method according to claim 1, wherein the reforming process comprises an autothermal reforming process and/or a partial oxidation reforming process.

Claim 3 (canceled).

4 (currently amended). The method according to ~~any preceding~~ claim 1, wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and

heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

5 (currently amended). The method according to ~~any preceding~~ claim 1, further comprising:

optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and

optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;

wherein the pre-reforming process comprises:

optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and

optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

6 (currently amended). The method according to ~~any preceding~~ claim 1, wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

outputting hydrogen from the permeate side of the Palladium membrane; and

outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

7 (currently amended). The method according to ~~any preceding~~ claim 1, wherein the hydrogen separation process comprises a PSA process.

Claims 8-10 (canceled).

11 (currently amended). The method according to ~~any of the preceding claims~~ claim 1, wherein the feed gas is natural gas.

12 (currently amended). The method according to ~~any of the preceding claims~~ claim 1, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.

13 (currently amended). The method according to claim 3, ~~or any claim dependent thereon,~~ 1 wherein the reforming process comprises a gas-heated reforming process and the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

14 (currently amended). The method according to ~~any preceding~~ claim 1, wherein the one or more reforming processes are supplied with oxygen from an air separation unit.

15 (currently amended). The method according to ~~any preceding~~ claim 1, wherein the water-gas-shift process is conducted in one water-gas-shift reactor;

wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C; and

wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

16 (currently amended). The method according to ~~any preceding~~ claim 1, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

17 (currently amended). The method according to ~~any preceding~~ claim 1, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

18 (currently amended). The method according to ~~any preceding~~ claim 1, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

19 (currently amended). The method according to ~~any preceding~~ claim 1, wherein water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

20 (currently amended). The method according to ~~any preceding~~ claim 1, wherein water is not separated from the shifted gas before the hydrogen separation process.

Claim 21 (canceled).

22 (currently amended). The method according to ~~any of the preceding claims~~ claim 1, wherein the carbon dioxide separation process is conducted cryogenically.

23 (currently amended). The method according to ~~any of the preceding claims~~ claim 1, the method further comprising generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

24 (currently amended). A hydrogen production plant arranged to perform ~~[[the]]~~ a method of any of claims 1 to 22 producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and

recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.

25 (currently amended). An ammonia production plant arranged to perform the ~~method of claim 23~~ a method of producing ammonia, the method comprising:

receiving a feed gas comprising hydrocarbons;

performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas;

recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;

wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%; and

generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

Application No. Not yet assigned  
Preliminary Amendment Dated September 1, 2022

### **REMARKS**

The present application is a U.S. National Stage of PCT International Patent Application No. PCT/EP2021/054441, filed February 23, 2021, which claims priority to GB Application Nos. 2003317.1, filed March 6, 2020, and 2010174.7, filed July 2, 2020.

Applicant submits herewith amendments to the specification and claims. The amendments to the specification address issues unique to U.S. practice, and do not add new matter to the application. Likewise, the amendments to the claims put the claims in better form for examination in the U.S. by reducing the number of claims to 20 claims total and 3 independent claims, by eliminating multiple dependencies, and by ensuring consistency. These amendments are not intended to introduce new matter.

If there is any matter that the Examiner would like to discuss, the Examiner is invited to contact the undersigned representative at the telephone number set forth below. In any event, the Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith to our Deposit Account No. 501039, under 2110-0010.

September 1, 2022

Respectfully submitted,

/Paul C. Craane/  
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## ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #  
**17/905,448**

RECEIPT DATE / TIME  
**09/01/2022 04:38:23 PM ET**

ATTORNEY DOCKET #  
**2110-0010**

### Title of Invention

HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### Application Information

|                        |                                                |                      |                       |
|------------------------|------------------------------------------------|----------------------|-----------------------|
| APPLICATION TYPE       | Utility - U.S. National Stage under 35 USC 371 | PATENT #             | -                     |
| CONFIRMATION #         | 8205                                           | FILED BY             | Paul Craane           |
| PATENT CENTER #        | 60932198                                       | FILING DATE          | -                     |
| CUSTOMER #             | 26568                                          | FIRST NAMED INVENTOR | Torkild R. Reinertsen |
| INTL. APPLICATION #    | PCT/EP2021/054441                              | INTL. FILING DATE    | 02/23/2021            |
| CORRESPONDENCE ADDRESS | -                                              | AUTHORIZED BY        | -                     |

### Documents

**TOTAL DOCUMENTS: 22**

| DOCUMENT                                | PAGES | DESCRIPTION                                                | SIZE (KB) |
|-----------------------------------------|-------|------------------------------------------------------------|-----------|
| 2110-0010-ADS.pdf                       | 10    | Application Data Sheet                                     | 2174 KB   |
| 2110-0010-Transmittal.pdf               | 4     | Transmittal of New Application                             | 309 KB    |
| 2110-0010-International_Application.pdf | 64    | Documents submitted with 371 (National Stage) Applications | 6408 KB   |
| 2110-0010-Declarations.pdf              | 6     | Oath or Declaration filed                                  | 10276 KB  |
| 2110-0010-IDS_Transmittal_Ltr.pdf       | 4     | Transmittal Letter                                         | 75 KB     |
| 2110-0010-IDS1449.pdf                   | 2     | Information Disclosure                                     | 71 KB     |



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|--------------------------------------------|----|-----------------------|---------|
| 2110-0010-FR2949772A1.pdf                  | 32 | Foreign Reference     | 4767 KB |
| 2110-0010-GB2571136A.pdf                   | 27 | Foreign Reference     | 5508 KB |
| 2110-0010-WO9112200A1.pdf                  | 20 | Foreign Reference     | 2421 KB |
| 2110-0010-WO2009088971A1.pdf               | 22 | Foreign Reference     | 2290 KB |
| 2110-0010-WO2019162236A1.pdf               | 39 | Foreign Reference     | 4213 KB |
| 2110-0010-WO2020012018A1.pdf               | 39 | Foreign Reference     | 3899 KB |
| 2110-0010-Combined_Search_Exam_Report1.pdf | 5  | Non Patent Literature | 548 KB  |
| 2110-0010-Combined_Search_Exam_Report2.pdf | 8  | Non Patent Literature | 871 KB  |
| 2110-0010-ISR_and_WO.pdf                   | 15 | Non Patent Literature | 1809 KB |
| 2110-0010-Rostrup-Nielsen_1993.pdf         | 20 | Non Patent Literature | 2697 KB |
| 2110-0010-Rostrup-Nielsen_2002.pdf         | 5  | Non Patent Literature | 242 KB  |
| 2110-0010-Preliminary_Amendment.pdf        | 10 | -                     | 98 KB   |

|                                           |         |   |                                                  |         |
|-------------------------------------------|---------|---|--------------------------------------------------|---------|
| 2110-0010-Preliminary__Amendment-A.PE.pdf | (1-1)   | 1 | Preliminary Amendment                            | 54 KB   |
| 2110-0010-Preliminary__Amendment-SPEC.pdf | (2-2)   | 1 | Specification                                    | 53 KB   |
| 2110-0010-Preliminary__Amendment-CLM.pdf  | (3-9)   | 7 | Claims                                           | 89 KB   |
| 2110-0010-Preliminary__Amendment-REM.pdf  | (10-10) | 1 | Applicant Arguments/Remarks Made in an Amendment | 55 KB   |
| 2110-0010-POA.pdf                         |         | 3 | Power of Attorney                                | 3100 KB |

## Digest

| DOCUMENT                                 | MESSAGE DIGEST(SHA-512)                                                                                                          |
|------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|
| 2110-0010-ADS.pdf                        | 12296D88E67C0307C1BAED97DB5B73A990D3253BB5507D1235A87382D568BF863E1EB142C17289E19125360DAAA7A706BC6A0658CC738AA0B17B4E9EBC6D7858 |
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| 2110-0010-International__Application.pdf | 1DB465DBC76585D12D15B2727A399D2CDF6E55A9B18A19E2CD1F5C620AD75BCFC3995BEBF4CCF926176D71D9EDA2E74270C1E4675B6C659DEF1BD9E392398CBC |
| 2110-0010-Declarations.pdf               | 7A6FC69A030EBEBBCFC6617345FB735E2C49FC41C8114BA8BB1662FFCF307A2FF65174B38C28582C32DD7F5637A4DCDEDC9D35FF118B156798510181C8362555 |

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| 2110-0010-FR2949772A1.pdf               | 290A1A83A83DF1795456416E09F0B6F718D385F59D53B1A4932B3369203F4E6F8D6A6753BB370F6EBFDBCF6D7E2F435CCE3ECC7A647FBC54EB6B238CF7219FB4  |
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| 2110-0010-WO9112200A1.pdf               | 9B40C83FCF9527463C38CABB2167296A1D166941B4C2B874AA33BE86318806453BFF02BF185F6F414EE08ABF1CA480CC35ADA5500078282FD0733DD92AFCFB87  |
| 2110-0010-WO2009088971A1.pdf            | E1CC1D54D0B927759E416F6FFCC6D3D7CF80A50216887CB25F7D96955BF3AB4384019322C30121864AB6CB609DD793C5E4E1E75B12BB3419F7FA0CC4126D5FA3  |
| 2110-0010-WO2019162236A1.pdf            | 7142463FCDFC8689CB687C28C19A929644261B8529D73B67F4748E513F43FCF31E0F601D6CB83D027908CCC4DA3367450B919682E1590AC9E1758455B665E7E7  |
| 2110-0010-WO2020012018A1.pdf            | 5C422C8D2487CCF24FE2BFE8A2C2D75EAB2DC048ED63066E517E7E70A7B86CA0C06E376EF766B246A35AD9453747A65958BAE7C4C576948D31033CE2343D227E  |
| 2110-0010-Combined_Search_Exam_Rpt1.pdf | 3DB2FF6903274117397C78373C1EF742F6A4E4AB47D4D15401FFB1587D99822E3008E560700C244F96317C6689B1B32F4AEB36AE26EAAEE75274FD21EA8AA7B09 |
| 2110-0010-Combined_Search_Exam_Rpt2.pdf | F0A143BF79F652AE4CF5BF8FFAC50E21B70CA03E91F67816E056C95D660ADB868B29D07695B9B176928E2F6DC19F9EED881874ED46360CA84FEDEE5741701F08  |

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| 2110-0010-Rostrup-<br>Nielsen_1993.pdf           | 56645EB869F99FCDDDB21E41FE9B31E15E5C379C8117456FE4<br>D156102ECECF30137003433D063C2A22A9193AB61C0FA12AB<br>44A54BA20AA005006E5CCC731CF235 |
| 2110-0010-Rostrup-<br>Nielsen_2002.pdf           | 2F6FC0C00119103FBF92EF7B732936CC1A00A0099BE662765A<br>62BDDEE670CA504DFA2DD15104E5E720735FCBEC1792FB8C<br>6C364AA8B3066990DD7DDA7EB4DC6E  |
| 2110-0010-<br>Preliminary_Amendment.pdf          | 657731996F8B0A86044EEA55AF4CD040C2509B36D9546BFE17<br>811A1598650F6D134BDFF368F7E15937C83064C5A69C399711<br>E417AFBEA6F1B0C9F751DAF4A3EC  |
| 2110-0010-<br>Preliminary_Amendment-<br>A.PE.pdf | 876573B6B7348D28784F618405DC141C5DDCCD5AC7DDA7A4<br>8CBA0C68C273E5BB0A14B44CD8D3223B3FB059D7A2AB9501<br>89DA468162057D9D363CA03DEC8FC4F9  |
| 2110-0010-<br>Preliminary_Amendment-<br>SPEC.pdf | 7B87FAC58D03D7E52AC6C76D7C46C79C82F90D20BB359D0B<br>AAD801EC558AC0F7855DC4D08119F634B91131C8D755377DB<br>1F72B9397EAAD6AEED1F12439280E35  |
| 2110-0010-<br>Preliminary_Amendment-<br>CLM.pdf  | 86D65856155B693C853C072CAF14983A15E2C00FCA7762BA2<br>F99E1D6094662502D8A51AE474CCBED843C3FE562199380B4<br>6C439129A5147F24A01E9BBCAE370B  |
| 2110-0010-<br>Preliminary_Amendment-<br>REM.pdf  | B8FD8B4F68F36CBF3E3D238FDCB587F0205C3FD36F840B557<br>1196E9F33E6AF04AA087217EDA6032050720F035F474F28DEE<br>C1CFB5439FC9D9AA68177AF8C802F  |
| 2110-0010-POA.pdf                                | 2093C66A4703C509B30BFF505DFDF657AAFD2D7E21AFA7792<br>B56FFD05A36F7835E20178647B8EC6FFA3DF699BDA86787952<br>C5A2CF023D3A1145089624430C2A9  |

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.

If a new application is being filed and the application includes the necessary components for 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.



## ELECTRONIC PAYMENT RECEIPT

APPLICATION #  
17/905,448

RECEIPT DATE / TIME  
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ATTORNEY DOCKET #  
2110-0010

### Title of Invention

HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### Application Information

|                        |                                                |                      |                       |
|------------------------|------------------------------------------------|----------------------|-----------------------|
| APPLICATION TYPE       | Utility - U.S. National Stage under 35 USC 371 | PATENT #             | -                     |
| CONFIRMATION #         | 8205                                           | FILED BY             | Paul Craane           |
| PATENT CENTER #        | 60932198                                       | AUTHORIZED BY        | -                     |
| CUSTOMER #             | 26563                                          | FILING DATE          | -                     |
| INTL. APPLICATION #    | PCT/EP2021/054441                              | INTL. FILING DATE    | 02/23/2021            |
| CORRESPONDENCE ADDRESS | -                                              | FIRST NAMED INVENTOR | Torkild R. Reinertsen |

### Payment Information

|                                  |                                                                                                                                                                         |                                      |
|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|
| PAYMENT METHOD<br>DA / 501039    | PAYMENT TRANSACTION ID<br>E202291G41461503                                                                                                                              | PAYMENT AUTHORIZED BY<br>Paul Craane |
| PRE-AUTHORIZED ACCOUNT<br>501039 | PRE-AUTHORIZED CATEGORY<br>37 CFR 1.492 (National application filing, search, and examination fees); 37 CFR 1.17 (Patent application and reexamination processing fees) |                                      |

| FEE CODE      | DESCRIPTION                                                              | ITEM PRICE(\$) | QUANTITY | ITEM TOTAL(\$) |
|---------------|--------------------------------------------------------------------------|----------------|----------|----------------|
| 1631          | BASIC NATIONAL STAGE FEE                                                 | 320.00         | 1        | 320.00         |
| 1633          | NATIONAL STAGE EXAMINATION FEE - ALL OTHER SITUATIONS                    | 800.00         | 1        | 800.00         |
| 1642          | NATIONAL STAGE SEARCH FEE - SEARCH REPORT PREPARED AND PROVIDED TO USPTO | 540.00         | 1        | 540.00         |
| TOTAL AMOUNT: |                                                                          |                |          | \$1,660.00     |

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**

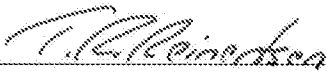
If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

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

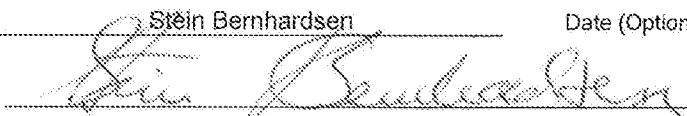
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition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

| DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                            |
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| <b>Title of Invention</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |
| <p>As the below named inventor, I hereby declare that:</p> <p>This declaration <input type="checkbox"/> The attached application, or<br/>is directed to: <input checked="" type="checkbox"/> United States application or PCT international application number <u>PCT/EP2021/054441</u><br/>filed on <u>February 23, 2021</u>.</p> <p style="margin-left: 100px;"><input type="checkbox"/> As Amended on _____ (if applicable)</p> <p>The above-identified application was made or authorized to be made by me.</p> <p>I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.</p> <p>I have reviewed and understand the contents of the above identified application, including the claims, as amended by an amendment, if any, specifically referred to herein. I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information that became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.</p> <p>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.</p> <p style="text-align: center;"><b>WARNING:</b></p> <p>Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identify theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.</p> |                                            |
| <p><b>LEGAL NAME OF INVENTOR</b></p> <p>Inventor: <u>Torkild R. Reinertsen</u> Date (Optional): <u>23/08/2022</u></p> <p>Signature: <u></u></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                            |
| <p><small>Note: An application data sheet (PTO/AIA/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/SB/AIA/01 form for each additional inventor.</small></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                            |



| DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                            |
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| <b>Title of Invention</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |
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| <p><b>LEGAL NAME OF INVENTOR</b></p> <p>Inventor: <u>Stein Bernhardsen</u> Date (Optional): <u>23.08.2022</u></p> <p>Signature: <u></u></p> <p><small>Note: An application data sheet (PTO/AIA/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/SB/AIA/01 form for each additional inventor.</small></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                            |

**DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN  
APPLICATION DATA SHEET (37 CFR 1.76)**

**Title of  
Invention**

HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

As the below named inventor, I hereby declare that:

This declaration ☐ The attached application, or  
is directed to:

☒ United States application or PCT international application number PCT/EP2021/054441  
filed on February 23, 2021.

☐ As Amended on \_\_\_\_\_ (if applicable)

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 application.

I have reviewed and understand the contents of the above identified application, including the claims, as amended by an amendment, if any, specifically referred to herein. I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information that 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.

**WARNING:**

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

**LEGAL NAME OF INVENTOR**

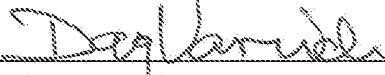
Inventor: Erling Rytter

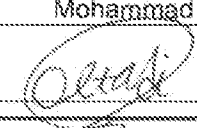
Date (Optional): Aug 24, 2020

Signature: Erling Rytter

Note: An application data sheet (PTO/AIA/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/SB/AIA/01 form for each additional inventor.

| DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN<br>APPLICATION DATA SHEET (37 CFR 1.76)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                            |
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| Title of<br>Invention                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |
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| <p><b>LEGAL NAME OF INVENTOR</b></p> <p>Inventor: <u>Dag Schanke</u> Date (Optional): <u>25.08.2022</u></p> <p>Signature: <u>Dag Schanke</u></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                            |
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| DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                            |
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| Title of Invention                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |
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| <p><b>LEGAL NAME OF INVENTOR</b></p> <p>Inventor: <u>Dag Vareide</u> Date (Optional): <u>2022/08/23</u></p> <p>Signature: <u></u></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                            |
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| DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                            |
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| Title of Invention                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS |
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| <p><b>LEGAL NAME OF INVENTOR</b></p> <p>Inventor: <u>Mohammad Ostadi</u> Date (Optional): <u>23. Aug. 2022</u></p> <p>Signature: </p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                            |
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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

|                                |   |                                    |
|--------------------------------|---|------------------------------------|
| In re application of:          | ) | Customer No.: 26568                |
|                                | ) |                                    |
| Torkild R. Reinertsen et al.   | ) | Confirmation No.: Not yet assigned |
|                                | ) |                                    |
| Serial No. Not yet assigned    | ) |                                    |
|                                | ) |                                    |
| Filed: February 23, 2021       | ) |                                    |
|                                | ) |                                    |
| Title: HYDROGEN AND/OR AMMONIA | ) |                                    |
| PRODUCTION PROCESS             | ) |                                    |
|                                | ) |                                    |
| Art Unit: Not yet assigned     | ) |                                    |
|                                | ) |                                    |
| Examiner: Not yet assigned     | ) |                                    |
|                                | ) |                                    |

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

**INFORMATION DISCLOSURE STATEMENT**

Dear Sir:

Pursuant to 37 CFR 1.56, 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the attached Form PTO-1449 (modified). It is respectfully requested that this information be expressly considered during the prosecution of this application, and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

In accordance with 37 CFR § 1.98(a)(2)(ii), Applicant has not submitted copies of the U.S. patents or publications. In accordance with 37 CFR § 1.98(a)(2), Applicant has submitted copies of the foreign patent and other (non-patent literature) documents.

Furthermore, in accordance with 37 CFR 1.98(a)(3) and MPEP 609.04(a) III., Applicant notes that French Pub. No. FR 2949772 was cited in the Combined Search and Examination Report (copy submitted herewith) by the UK Intellectual Property Office in counterpart App. No. GB 2010174.7, which search and examination report indicates the degree of relevance found by the UKIPO. Applicant also notes that PCT Pub. No. WO 91/12200 was cited in the Combined Search and Examination Report (copy submitted herewith) by the UKIPO in counterpart App. No. GB 2003317.1, which search and examination report indicates the degree of relevance found by the UKIPO. In addition, English-language machine translations of French Pub. No. FR 2949772 and PCT Pub. No. WO 91/12200 are provided herewith.

In accordance with 37 CFR 1.97(g), the filing of this Information Disclosure Statement shall not be construed to mean that a search has been made or that no other material information as defined by 37 CFR 1.56(a) exists. In accordance with 37 CFR 1.97(h), the filing of this Information Disclosure Statement shall not be construed to be an admission that any patent, publication, or other information referred to therein is “prior art” for this invention unless specifically designated as such.

Further, no inference should be drawn that any disclosure is equivalent to the subject invention. Citation of any document herein is not to be construed as an admission that any subject matter disclosed in the document is necessarily within the inventive field of endeavor, that any disclosure is necessarily prior in time to a particular date which may be relevant to the instant patent application, and/or that any disclosure is otherwise necessarily prior art with respect to the instant invention.

The right is also reserved to later set forth how the instant invention is distinguished over the disclosure of any document or other art, including the disclosure

of those documents discussed herein, that may be cited by the Examiner in rejecting a claim in the present patent application.

- ☒ 1. This Information Disclosure Statement is being filed within the following time period(s) set forth in 37 CFR § 1.97(b), and therefore no fee is believed to be due:
- ☐ Within three months of the filing date of a national application other than a continued prosecution application under § 1.53(d);
  - ☒ Within three months of the date of entry of the national stage as set forth in § 1.491 in an international application;
  - ☐ Before the mailing of first Office action on the merits; or
  - ☐ Before the mailing of first Office action after the filing of a request for continued examination under § 1.114.
- ☐ 2. As set forth in 37 CFR § 1.97(c), this Information Disclosure Statement is being filed after the time period set forth in 37 CFR § 1.97(b) (see above) but before the mailing date of any of a final action under 37 CFR § 1.113, a notice of allowance under 37 CFR § 1.311 or an action that otherwise closes prosecution in the application. [Select either one of the statements OR the fee below, as appropriate.]
- ☐ It is hereby stated and certified with respect to this Information Disclosure Statement:
- ☐ 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; 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 § 1.56(c) more than three months prior to the filing of the Information Disclosure Statement.
- ☐ Enclosed is the fee set forth in 37 CFR § 1.17(p) or in the event no fee is enclosed, this is a request and authorization to charge the appropriate fee to Deposit Account No. 50-1039.



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In summary, it is respectfully requested that this Information Disclosure Statement be considered and made of record, and that any fee required for consideration, if not authorized above, be charged to deposit account no. 50-1039.

Respectfully submitted,

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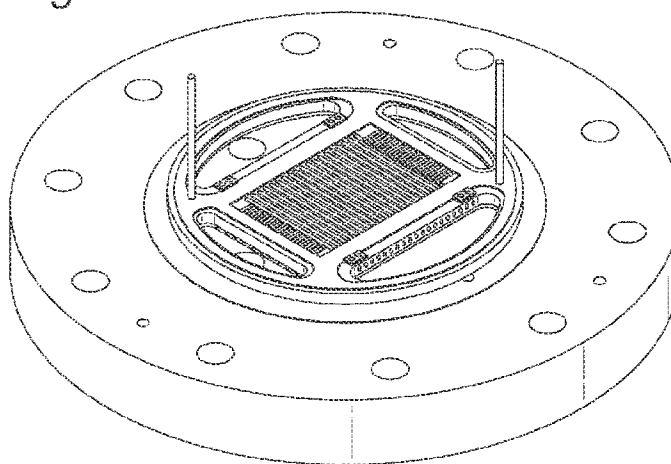
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## (54) Title: GAS SEPARATION DEVICE

Fig. 4B



(57) Abstract: Disclosed herein is a gas separation section for separating a first gas from one or more other gasses in a separation device, the gas separation section comprising: a first membrane that is substantially planar; a second membrane that is substantially planar; a first substrate that has a first surface and a second surface, wherein the second surface of the first substrate is on an opposite side of the first substrate than the first surface of the first substrate; a second substrate that has a first surface and a second surface, wherein the second surface of the second substrate is on an opposite side of the second substrate than the first surface of the second substrate; and a mesh that is arranged between the second surface of the first substrate and the second surface of the second substrate; wherein: the first substrate and the second substrate are sintered plates; the first membrane is on the first surface of the first substrate; the second membrane is on the first surface of the second substrate; the first and second membranes are both permeable by at least a first gas and not permeable by one or more other gasses; the thickness of the first membrane in a direction orthogonal to the plane of the first membrane is less than 10 micrometres; and the thickness of the second membrane in a direction orthogonal to the plane of the second membrane is less than 10 micrometres. Embodiments provide an improved gas separation device over known techniques. Advantages of the separation device according to embodiments include improved performance, easy implementation, a modular design

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and a scalable design.

## Gas Separation Device

### Abstract

5 The present invention relates to the separation of gases by membranes. Embodiments provide a separation device that is particularly appropriate for the separation of hydrogen from syngas. Advantages of the separation device according to embodiments include improved performance over known separation devices, easy implementation, a modular design and a scalable design.

10

### Background

Hydrogen is increasingly being used as an energy source. An advantage of hydrogen is that it combusts to produce water and it is therefore a clean fuel. Applications in which  
15 hydrogen may be used as a combusted fuel include the powering of ships and as a domestic gas supply. Hydrogen may also be used in fuel cells that are an environmentally friendly alternative to conventional batteries.

An efficient form of hydrogen production is from syngas. Syngas may be produced by  
20 reforming natural gas. Syngas is a gas mixture that mostly comprises carbon monoxide and hydrogen. Syngas may also comprise amounts of carbon dioxide and other gasses, such as methane. A water gas shift reaction may also be performed on the syngas in order to increase the concentration of hydrogen in the gas mixture. To produce substantially  
25 pure hydrogen, it is necessary to separate the hydrogen from the other gasses in the gas mixture.

A known technique for separating hydrogen from other gasses is the use of a palladium alloy membrane. A gas mixture is passed through a pipe with the membrane as the pipe walls. The hydrogen diffuses through the membrane and is thereby separated from the  
30 other gasses in the gas mixture that are unable to pass through the membrane.

In known hydrogen separators, the membrane thickness is typically in the order of 100 micrometres. The rate at which hydrogen can pass through the membrane is inversely proportional to the membrane thickness and proportional to the membrane surface area. The separation of hydrogen by such membranes is slow due to the large membrane  
5 thickness. In addition, the implementation costs are high because palladium is expensive.

There is a general need to improve known gas cleaning and/or separation devices.

### Summary

10

According to a first aspect of the invention, there is provided a gas separation section for separating a first gas from one or more other gasses in a separation device, the gas separation section comprising: a first membrane that is substantially planar; a second membrane that is substantially planar; a first substrate that has a first surface and a second  
15 surface, wherein the second surface of the first substrate is on an opposite side of the first substrate than the first surface of the first substrate; a second substrate that has a first surface and a second surface, wherein the second surface of the second substrate is on an opposite side of the second substrate than the first surface of the second substrate; and a mesh that is arranged between the second surface of the first substrate and the second  
20 surface of the second substrate; wherein: the first membrane is on the first surface of the first substrate; the second membrane is on the first surface of the second substrate; the first and second membranes are both permeable by at least a first gas and not permeable by one or more other gasses; the thickness of the first membrane in a direction orthogonal to the plane of the first membrane is less than 10 micrometres; and the thickness of the second  
25 membrane in a direction orthogonal to the plane of the second membrane is less than 10 micrometres.

Preferably, the first gas is hydrogen and the one or more other gasses include carbon monoxide and/or carbon dioxide.

30

Preferably, the first and second membranes comprise palladium; and, optionally, the first and second membranes further comprise one or more other metals than palladium.

Preferably, the first and/or second membrane comprises silver; and, preferably, the membrane is between 15 wt% to 40 wt% silver with the rest of the membrane being palladium; and, more preferably, the membrane is 77 wt% palladium and 23 wt% silver.

5

Preferably, said thickness of the first and/or second membrane is between 0.2 and 4 micrometres, preferably between 1 and 3 micrometres.

Preferably, the first and second membranes are substantially square shaped.

10

Preferably, the mesh is a steel mesh.

Preferably; the mesh is attached to the second surface of the first substrate at a plurality of locations between opposite edges of the second surface of the first substrate; and the mesh is attached to the second surface of the second substrate at a plurality of locations between opposite edges of the second surface of the second substrate.

15

Preferably, the mesh is arranged to maintain the second surface of the first substrate substantially parallel to the second surface of the second substrate.

20

Preferably, the mesh is arranged to maintain the second surface of the first substrate separated from the second surface of the second substrate by a distance in the range 2 mm to 30 mm.

25 Preferably, the first and/or second substrates comprise any of a sintered plate, metal, ceramics, polymer or combinations thereof.

Preferably, said thickness of the first and/or second substrate is less than 3mm.

30 Preferably, the gas separation device further comprises: a first gasket that is arranged to provide a gas seal at the edges of the first membrane; and a second gasket that is arranged to provide a gas seal at the edges of the second membrane.

Preferably, the mesh is arranged in a channel that, in use, the first gas is arranged to flow through.

5 Preferably, the gas separation device further comprises a frame that is arranged to contain a flow path of the first gas; wherein the frame arranged to be in fluid communication with the channel such that, in use, the first gas flows from the channel into the frame.

Preferably, the frame comprises a substantially annular section that encircles the first and second membranes.

10

Preferably; the first gasket is a single piece structure that comprises a substantially square section within a substantially annular section; and/or the second gasket is a single piece structure that comprises a substantially square section within a substantially annular section.

15

According to a second aspect of the invention, there is provided a separation device for separating a first gas from one or more other gasses, the separation device comprising: an inlet for receiving a gas mixture comprising a first gas and one or more other gasses; a plurality of gas separation sections according to the first aspect of the invention, wherein

20 the plurality of gas separation sections are arranged in a stack; a first outlet arranged to output the first gas that has passed through one or more of the membranes in the one or more gas separation sections; and a second outlet arranged to output at least the one or more other gasses that have not passed through one or more of the membranes in the one or more gas separation sections.

25 Preferably, the plurality of gas separation sections are arranged in a vertical stack.

Preferably, the separation device further comprises an outer housing; and the plurality of gas separation sections are arranged within the outer housing.

30

Preferably, the outer housing is substantially cylindrical.

Preferably, the first inlet is provided in either an upper or a lower section of the housing, such that, in use, the direction of flow of the gas mixture into the housing is substantially orthogonal to the planes of the membranes in the gas separation sections.

- 5     Preferably, the housing further comprises an inlet that is arranged to receive steam for heating the gas separation sections.

Preferably, the housing further comprises an inlet for purge gas that is supplied to one or more channels that the first gas that has passed through a membrane is arranged to flow  
10     through.

According to a third aspect of the invention, there is provided a method of separating a first gas from a gas mixture comprising the first gas and one or more other gasses, the method comprising: feeding the gas mixture into a separation device according to the second  
15     aspect of the invention; receiving first a gas flow from the separation device that comprises substantially only the first gas; and receiving a second gas flow from the separation device that comprises at least the one or more other gasses than the first gas.

#### **List of figures**

20

Figure 1 shows a known implementation of an apparatus for separating hydrogen from other gasses;

Figure 2 is a cross-section of components of part of a separation device according to an  
25     embodiment;

Figure 3A shows part of an implementation of a single gas separation section according to an embodiment;

30     Figure 3B shows part of an implementation of a single gas separation section according to an embodiment;



Figure 3C shows two gas separation sections, with one stacked on top of the other, according to an embodiment;

Figure 4A shows the components of a gas separation device and a base according to an  
5 embodiment;

Figure 4B shows the components of a gas separation device provided on a base according to an embodiment;

10 Figure 5 shows a cross section through a separation device according to an embodiment;

Figure 6A shows a separation device according to an embodiment; and

Figure 6B shows a separation device according to an embodiment.  
15

### **Embodiments**

Embodiments provide an improved gas separation device over known techniques. Advantages of the separation device according to embodiments include improved  
20 performance, easy implementation, a modular design and a scalable design.

Figure 1 shows a known implementation of an apparatus for separating hydrogen from other gasses. The apparatus shown in Figure 1 is disclosed in Figure 6 of US8,163,064 B2. An important advantage of the apparatus shown in Figure 1 over other known hydrogen  
25 separation techniques is that the thickness of the palladium membrane is reduced to less than 10 micrometres. The reduced thickness of the membrane both increases hydrogen flow through the membrane and reduces costs.

Embodiments provide a hydrogen separation device that improves on the apparatus shown  
30 in Figure 1.

Figures 6A and 6B show a separation device 500 according to embodiments.

Figure 2 is a cross-section of components of part of a separation device 500 according to an embodiment. The separation device 500 is described in the example application of hydrogen separation from syngas. A water gas shift reaction may have been performed on the syngas and so the reference to syngas is to be understood as being any gas mixture comprising hydrogen and one or more of carbon monoxide, carbon dioxide, steam and other gasses, such as methane. As shown by the text in the large arrows in Figure 2, embodiments include the input gas mixture being substantially a mixture of only carbon dioxide and hydrogen. A first output may be a stream of substantially only carbon dioxide. A second output, that is separate from the first output, may be a stream of substantially only hydrogen.

The separation device 500 comprises a plurality of first channels 202 and a plurality of second channels 204. Each of the first channels 202 are formed between planar membranes 201 that are walls of the first channel 202. Each planar membrane 201 is formed on a substrate 203 that supports the membrane 201. Each substrate 203 is formed on a steel mesh on the other side of the substrate 203 from the membrane 201. The mesh is provided within each of a plurality of second channels 204. Hydrogen is able to pass through the membrane 201, pass through the substrate 203 and flow along each second channel 204, as the mesh structure comprises gas flow paths for the hydrogen.

The gas input to each of the first channels 202 is syngas. The gas that is output from each of the first channels 202 is referred to herein as a retentate gas. Retentate gas is the remaining contents of the input syngas into a first channel 202 after some, or all, of the hydrogen in the input syngas gas has passed through a membrane 201. The output gas from a second channel 204 comprises hydrogen that has passed through a membrane 201.

Each first channel 202 has an inlet 205 for syngas at one end of the channel and an outlet 206 for retentate at the other end of the first channel 202.

30

At least one end of each second channel 204 is an outlet 207 for hydrogen. Embodiments also include more than one end of the second channel 204 being an outlet for hydrogen.

In use, syngas is provided at the inlet of one or more of the first channels 202 and passes through each of these first channels 202 towards the respective outlets of the first channels 202. As the syngas passes through each first channel 202, hydrogen in the syngas passes  
5 through the planar membrane 201 walls of the channel. The retentate gas that passes through the outlet of each first channel 202 has a lower concentration of hydrogen than the syngas gas at the inlet of the first channel 202 due to the hydrogen passing through the membrane 201. Preferably, substantially no hydrogen is present in the gas that passes through the outlet of each first channel 202. The hydrogen that passes through the  
10 membrane 201 passes through the substrate 203, into one of the second channels 204 and out of an outlet 207 of the second channel 204.

Figures 3A and 3B show part of an implementation of a single gas separation section 300 of a separation device 500 according to an embodiment. Figure 3C shows two gas  
15 separation sections 300 with one stacked on top of the other. Figure 4A shows the components of a gas separation section 300 together with a base 402 that the gas separation section 300 is provided on according to an embodiment. Figure 4B shows the gas separation section 300 in Figure 4A when formed and provided on the base 402. When the separation device 500 is orientated so that each of the membranes 201 is horizontal, the  
20 base 402 may be either an upper section or a lower section of the gas separation device 500.

The separation device 500 according to embodiments preferably comprises a plurality of gas separation sections 300, as shown in at least Figures 3C and 5.

25 Gas separation sections 300, as shown in Figures 3A, 3B, 4A and 4B, provide the parts of the structure as described earlier with reference to Figure 2. Each gas separation section 300 comprises two planar membranes 201 with each planar membrane 201 provided on a side of a substrate 203. The other side of each substrate 203 is connected to a steel mesh.  
30 The mesh defines a second channel 204 between the membranes 201 for collecting hydrogen.

As shown in at least Figures 3C, 4B and 5, each gas separation section 300 is a substantially planar structure that comprises a substantially annular part as well as a substantially square part. The membranes 201 are provided in the substantially square part of each gas separation section 300. Each gas separation section 300 has one or more  
5 connecting sections between the substantially square part and the substantially annular part. For example, a connecting section may be provided at each of the four corners of the square part, as shown in at least Figures 3C and 4B.

As shown in at least Figures 3C, 4B and 5, there is a segment shaped hole between each  
10 outer edge of the substantially square part of each gas separation section 300 and the inner edge of the substantially annular part of each gas separation section 300. Each gas separation section 300 comprises four separate segment shaped holes, with each of the segment shaped holes having substantially the shape of a segment of a circle.

15 Each gas separation section 300 comprises a hydrogen frame 301. The hydrogen frame 301 provides a structural support for a mesh. The mesh supports a substrate 203 and the substrate 203 supports a membrane 201.

Each hydrogen frame 301 is a substantially planar structure that comprises a substantially  
20 annular part as well as a substantially square part. Between each outer edge of the substantially square part of each hydrogen frame 301 and the inner edge of the substantially annular part of the hydrogen frame 301 is a segment shaped hole, the hydrogen frame 301 comprising four such segment shaped holes. There are circular holes through opposing side walls of the substantially square part of each hydrogen frame 301  
25 such that each hydrogen frame 301 provides a flow path of hydrogen out of a second channel 204 that is formed within the substantially square part of the hydrogen frame 301. The direction of the flow path of hydrogen through the circular holes of the side walls of the substantially square part of the hydrogen frame 301 is parallel to the plane of the hydrogen frame 301. In use, hydrogen within the second channel 204 is therefore able to  
30 flow out of the second channel 204 and into at least one of the segment shaped holes of the hydrogen frame 301.

As shown in at least Figure 4A, each gas separation section 300 also comprises a syngas frame 404. Each syngas frame 404 is a substantially planar structure that comprises a substantially annular part as well as a substantially square part. Between each outer edge of the substantially square part of each syngas frame 404 and the inner edge of the

5 substantially annular part of the syngas frame 404 is a segment shaped hole, the syngas frame 404 comprising four such segment shaped holes. There are circular holes through opposing side walls of the substantially square part of each syngas frame 404 such that each syngas frame 404 provides a flow path of the syngas into a first channel 202 and the retentate gas, i.e. syngas without the hydrogen that has flowed through a membrane 201,

10 out of the first channel 202. The direction of the flow path of syngas and retentate gas through the circular holes of the side walls of the substantially square part of the syngas frame 404 is parallel to the plane of the syngas frame 404. The first channel 202 is formed between two adjacent gas separation sections 300 that are in a stacked arrangement, as shown in at least Figure 3C. When three or more gas separation sections 300 are in a

15 stacked arrangement, two or more first channels 202 are formed, as shown in, and described with reference to, Figure 2. Each first channel 202 is formed between the substantially square parts of two syngas frames 404. In use, retentate gas within each first channel 202 is therefore able to flow out of the first channel 202 and into at least one of the segment shaped holes of a syngas frame 404.

20 The syngas frames 404 and hydrogen frames 301 have a similar shape to each other. Each segment shaped hole of each syngas frame 404 has substantially the same shape as, and is aligned with, a segment shaped hole of a hydrogen frame 301. Each segment shaped hole of each gas separation section 300 therefore comprises the segment shaped hole of at least

25 one hydrogen frame 301 and the segment shaped hole of at least one syngas frame 404. Both the hydrogen frame 301 and the syngas frame 404 comprise circular holes, in an opposing pair of the side walls of their substantially square parts, for providing gas flow paths. The hydrogen frame 301 and a syngas frame 404 within a gas separation section 300 are positioned such that the pair of opposing walls of the hydrogen frame 301 that

30 comprise the circular holes are not aligned with the pair of opposing walls of the syngas frame 404 that comprise circular holes. The direction of the gas flow path provided by the circular holes of the hydrogen frame 301 is therefore orthogonal to the direction of the gas

flow path provided by the circular holes of the syngas frame 404. When a plurality of gas separation sections are stacked on top of each other, all of the hydrogen frames 301 and the syngas frames 404 of the gas separation sections are aligned with each other such that the directions of the gas flow paths provided by the circular holes of all of the hydrogen frames 301 are the same and the directions of the gas flow paths provided by the circular holes of all of the syngas frames 404 are the same.

The segment shaped holes in each gas separation section 300 are not in direct fluid communication with each other. Gas in one of the segment shaped holes can only flow into a different one of the segment shaped holes by flowing through a first channel 202 or a second channel 204.

As shown in Figures 3A, 3B, 4A and 4B, gaskets 303 are provided. Gaskets 303 are gas seals. A gasket 303 is provided that covers all of the edges of each membrane 201 so that gas in the first channel 202 is prevented from flowing around the ends of the membrane 201 into the second channel 204, and vice versa. The only gas flow between the first channel 202 and second channel 204 is therefore gas that has passed through the membrane 201, and not around the edges of the membrane 201. Each gasket 303 is preferably a single structure that provides a gas seal around all of the edges of the membrane 201. Each gasket 303 is preferably integral with the upper, or lower, section of a hydrogen frame 301.

Between adjacent gas separation sections 300 a gas tight seal, e.g. a polymeric/rubber seal, may be provided for preventing any undesired gas flow paths.

As shown in at least Figure 4A, each gas separation section 300 may be formed by positioning different components of the gas separation section 300 on each other. A gas separation section 300 may be formed on a base 402 that comprises a flange. A first gasket 303, that may have substantially the same shape as each hydrogen frame 301 and syngas frame 404, may be positioned directly on the base 402. A syngas frame 404 may be positioned on the first gasket. A hydrogen frame 301 may be positioned on the syngas frame 404. The hydrogen frame 301 supports a steel mesh. The mesh supports two substrates 203 and each substrate supports a membrane 201. In Figure 4A, an upper

substrate 203 and membrane 201 is shown. A lower substrate 203 and membrane 201 is also present, however this is not visible in Figure 4A. Although not shown in Figure 4A, another gasket, with a similar shape to the first gasket, may be provided between the syngas frame 404 and the hydrogen frame 301. One or more guide pins 403 may be  
5 provided for aiding the alignment of each of the components of all of the gas separation sections 300.

A first implementation of a gas separation section 300 according to an embodiment is shown in Figures 3A, 3B and 3C. A second implementation of a gas separation section  
10 300 according to an embodiment is shown in Figures 4A and 4B.

As shown in at least Figure 3C, in the first implementation a gasket is attached to a hydrogen frame 301 by at least one, and preferably two, cuboid bar shaped member. Each cuboid shaped bar member substantially extends along the entire length of an edge of the  
15 substantially square shaped part of the hydrogen frame 301. As shown in at least Figures 4A and 4B, the second implementation differs from the first implementation by the gasket being attached to a hydrogen frame 301 by at least one short gasket retainer. Preferably, there are four gasket retainers as shown on at least Figure 4B. Each gasket retainer may be  
20 screwed to the hydrogen frame 301.

As shown in at least Figure 5, when a plurality of gas separation sections 300 are arranged in a stack, the segment shaped holes of each gas separation section 300 are aligned with each other such that gas in the segment shaped hole of each gas separation section 300 can flow directly into a corresponding segment shaped hole of at least one other adjacent gas  
25 separation section 300. Due to the alignment of the gas separation sections 300, gas is prevented from directly flowing from a segment shaped hole of a gas separation section 300 into more than one segment shaped hole of an adjacent gas separation section 300.

The segment shaped holes of the plurality of gas separation sections 300 align to form four  
30 inlet/outlet channels 501, 502, 503, 504 through the stack of gas separation sections 300. Each inlet/outlet channel 501, 502, 503, 504 may be in fluid communication with at least one input or output port of the separation device 500. The inlet/outlet channels may

therefore provide flow paths for the input syngas, the output hydrogen and the output retentate gas. Although not shown in Figure 5, each of the gas separation sections 300 in Figure 5 has the above-described circular holes in its hydrogen frame 301 and its syngas frame 404. All of the gas separation sections are aligned such that each channel 501, 502, 503, 504 is a parallel arrangement of the same gas inlet/outlet of substantially identical gas separation sections.

For example, channel 502 may be an inlet channel that provides a flow path of syngas from an input port for syngas. The syngas may flow into and along channel 502, in a direction that is orthogonal to the plane of each gas separation section 300, and into any of the gas separation sections 300. All of the inlets of syngas into the first channels 202 of the plurality of gas separation sections 300 are in parallel with each other.

Channel 503 may be an outlet channel that provides a flow path of the retentate gas to an output port for retentate gas. The retentate gas flows out of each first channel 202 into channel 503 and then, in a direction that is orthogonal to the plane of each gas separation section 300, along channel 503 to an output port. All of the outlets of retentate gas from the first channels 202 of the plurality of gas separation sections 300 are in parallel with each other.

One, or both, of channels 501 and 504 may be outlet channels of hydrogen that provide flow paths of hydrogen to one or more outputs for hydrogen. The hydrogen may flow out of each second channel 204 into at least one, or both, of channels 501 and 504, and then, in a direction that is orthogonal to the plane of each gas separation section 300, along one, or both, of channels 501 and 504 to at least one output port for hydrogen. All of the outlets of hydrogen from the second channels 204 of the plurality of gas separation sections 300 are in parallel with each other.

In an alternative embodiment, channel 501 provides an outlet channel of hydrogen and channel 504 provides an inlet channel of purge gas. The purge gas flows into each second channel 204. The purge gas increases the rate at which hydrogen that has passed through the membrane 201 flows out of a second channel 204 into a hydrogen frame 301. This



reduces the partial pressure of the hydrogen in the second channel 204 and therefore increases the rate at which hydrogen travels from the first channel 202 into the second channel 204 via the membrane 201.

- 5     Figures 5, 6A and 6B show a separation device 500 according to an embodiment. Figure 5 is a cross section through the separation device 500 according to an embodiment.

As shown in Figures 6A and 6B, the separation device 500 comprises an annular outer chamber, a circular upper section and a circular lower section. The upper section and/or  
10     the lower section may be bases 402 for a gas separation section 300. As shown in Figure 5, the separation device 500 comprises a plurality of gas separation sections 300 in a stacked configuration. The plurality of gas separation sections 300 may be vertically stacked so that each plane of a membrane 201 is horizontal. As shown in Figure 6B, the upper section and lower section may be bolted together by bolts that pass through flanges  
15     of both the upper section and the lower section.

Provided in one, or both, ends of the separation device 500, that may be an upper or lower section of the separation device 500, are at least one input port for syngas and at least one output port for retentate.  
20

Provided in one, or both, ends of the separation device 500, that may be an upper or lower section of the separation device 500, are one or more output ports for hydrogen and/or a mixture of hydrogen and purge gas. There may be at least one input port in the separation device 500 for a purge gas in an upper and/or lower section of the separation device 500.  
25

There may also be one or more input and/or output ports in the separation device 500 for other gasses, in particular for steam. The one or more input and/or output ports for steam may be in an upper and/or lower section of the separation device 500. Steam is preferably fed into the separation device 500 in order to heat the membranes 201. Alternatively, or in  
30     addition, the separation device 500 may be heated in other ways, such as electrically.

The outer housing of the separation device 500 advantageously allows the separation of the hydrogen and syngas to be performed in a heated and pressurised environment. The presence of a cylindrical outer housing also increases the safety of the system.

- 5     The membrane 201 according to embodiments is less than 10 micrometres thick. That is to say, in a distance orthogonal to the plane of the membrane 201, the planar surfaces of the membrane 201 are less than 10 micrometres apart from each other.

10     The membrane 201 is preferably between 1 and 4 micrometres thick, more preferably between 2 and 3 micrometres thick.

The membrane 201 according to embodiments may be the same as, and manufactured in the same way as, the membranes disclosed in US8,163,064 B2 and/or US6,086,729.

- 15     The composition of the membrane 201 may be substantially only palladium. Alternatively, the membrane 201 may comprise palladium and one or more other metals than palladium.

20     The composition of the membrane 201 is preferably such that between 15% and 40% of its weight is silver with the rest of the weight being palladium. Preferably, the composition of the membrane 201 is such that between a fifth and a third of its weight is silver with the rest of the weight being palladium. More preferably, the composition of the membrane 201 is such that 77% of its weight is palladium and 23% of its weight is silver.

25     The membrane 201 may comprise palladium, silver and metal X and/or metal Y, where metal X is different from metal Y, and metal X and metal Y are both other metals than palladium and silver.

30     The membrane 201 is preferably square, with the length of each side of the square being about 500mm.

The substrate 203 according to embodiments has the property that hydrogen can pass through it. The substrate 203 may be either a porous material or a material that is

penetrable by hydrogen due to solid phase diffusion (e.g. mixed conductors of electronic and oxygen ion conducting and/or proton conducting cerams or metals of the IVB and VB groups) or layered combinations thereof. The substrate 203 may be made from metal, ceramic, polymer, or combinations thereof.

5

In a particularly preferred embodiment, the substrate 203 is a sintered plate. The sintered plate may be manufactured from steel, preferably AISI316L. A sintered plate is a particularly preferred substrate for a thin membrane 201, such as the membranes disclosed in US8,163,064 B2 and/or US6,086,729.

10

The membrane 201 is preferably provided directly on the substrate 203. That is to say, there is no further layer of material provided between the membrane 201 and the substrate 203. This minimises the transportation distance, and transportation resistance, of hydrogen between the first channel 202 and the second channel 204.

15

The substrate 203 may be between 0.5 mm and 5 mm thick, preferably between 1 mm and 3 mm thick.

The planar surfaces of the substrate 203 should be at least the same size as the planar membrane 201 that it supports, and are preferably substantially the same size as the membrane 201. The substrate 203 therefore preferably has square planar surfaces, with the length of each side of the square being 500mm.

20

The number of gas separation sections 300 in the separation device 500 is variable and may be in the range 2 to 500, preferably 25 to 200.

25

The separation device 500 preferably is designed to operate at pressures of at least 50 barg.

The separation device 500 preferably is designed to operate at temperatures of at least 450 °C.

30

The separation device 500 preferably has a typical operational temperature in the range 300 °C to 400 °C.

5 The outer diameter of each gas separation section 300 may be in the range 710 mm to 1000 mm.

The outer diameter of the housing may be in the range 750 mm to 1200 mm.

10 The height of the housing may be in the range 350 mm to 5000 mm.

The height of the upper and/or lower section of the housing may be in the range 50 mm to 200 mm.

15 The mesh may be shaped so as to maintain the substrates 203 that it is attached to parallel to each other and spaced apart by a distance in the range 1 mm to 100mm, preferably in the range 2 mm to 30 mm.

The flow rate of syngas into the separation device 500 may be 10 000 Nm<sup>3</sup>/h.

20 The above-provided dimensions of the components of the separation device 500 are approximate and embodiments also include variations to these dimensions. For example, the shapes of components may be varied so as to accommodate instrumentation into the separation device 500. The separation device 500 may also be made in a range of sizes so that the it is appropriate for both small and large scale applications.

25 The separation device 500 according to embodiments is advantageously easy to implement and suitable for large scale hydrogen separation from syngas.

30 The rate at which hydrogen can be separated from syngas by a separation device 500 according to embodiments can be easily changed by increasing, or reducing, the number of gas separation sections 300 within the outer housing.

The separation device 500 is also easily scalable. The rate at which hydrogen can be separated from syngas can be increased by increasing the height of the outer housing so that it may comprise a larger number of gas separation sections 300.

- 5     The separation device 500 also has a modular design. Any of the gas separation sections 300 within the separation device 500 can be easily accessed and replaced if a fault has occurred or for inspection/maintenance.

10     The input and output ports are preferably also orientated perpendicular to the main flow paths through each of the first and second channels 204 through the separation device 500. The inputs and outputs of each first channel 202 are therefore in parallel with each other. The variation of the amount of syngas that flows into each first channel 202 is therefore small. Advantageously, a complicated electronically controlled manifold system is not required for ensuring that the flow rate of syngas into each of the first channels 202 is  
15     appropriate. The flow rate of syngas into each of the first channel 202 also remains appropriate when the number of gas separation sections 300 is changed.

20     The parallel inputs of syngas to each first channel 202 is advantageous over providing a flow path so that all of the first channels in series with each other. When the inputs of first channels 202 are in parallel, the concentration of hydrogen in the syngas is the same for each first channel 202. When the first channels are in series with each other, the concentration of hydrogen in the syngas is different for each first channel.

25     Another advantage of the gas separation sections 300 according to embodiments is the use of a mesh. The mesh in each gas separation section 300 provides the main structural support for the substrates 203 and membranes 201. The mesh therefore allows use of thin substrates 203 as each substrate 203 needs only be thick enough to support a membrane 201 and to be attachable to the mesh. It is not necessary for the substrates 203 to be thick enough to provide the structural support of the second channel 204 through a gas  
30     separation section 300. Reducing the thickness of the substrates 203 both reduces the required spacing between membranes 201 and reduces the manufacturing cost.

The outer housing of the separation device 500 advantageously allows all of pressurised operation, the use of steam and increases safety.

5 The apparatus as shown in Figure 1 has a number of fundamental design differences from separation devices 500 according to embodiments. A consequence of these differences is that the membrane module as shown in Figure 1 is not easy to implement and is not suitable for large scale hydrogen separation from syngas.

10 In Figure 1, there is no mesh connecting substrates. Each substrate therefore needs to be strong enough to structurally support channels through the membrane module. As a consequence, the substrates need to be thick and this increases the size and cost of the membrane module.

15 In addition, spacers are required between the membranes for maintaining the separation between the membranes. Providing spacers on the membrane as shown in Figure 1 increases the likelihood of the membrane being damaged. The spacers also impede the flow of syngas between the membranes.

20 The membrane module shown in Figure 1 does not comprise a gasket 303 at the edge of the membrane. There would therefore be a risk of gas leakage at the ends of the membrane.

25 The membrane module shown in Figure 1 does not comprise an outer housing. It is therefore not possible to pressurise and heat the membranes.

The membrane module shown in Figure 1 is not scalable. The input and output ports of the syngas are provided in the same plane as the membranes and at the vertical mid-point of the structure. If the number of membranes is increased to above two, the flow of syngas will not be equally distributed amongst the membranes.

30

In addition, in Figure 1 the input flow of syngas is directly onto the membrane structures. If the flow rate of the syngas is increased, the increased flow may damage the membrane structures that the syngas flows onto.

- 5     The membrane module shown in Figure 1 does not have a modular design. The number of membranes cannot be changed and the membranes cannot be easily replaced.

The separation device 500 according to embodiments also has a number of advantages over other types of known separation devices from that shown in Figure 1. In particular,  
10     the membrane 201 according to embodiments is thin. The membrane 201 is preferably less than 10 micrometres thick, more preferably between 1 and 5 micrometres thick. Other types of known separation devices from that shown in Figure 1 have thicker membranes. The rate of flow of hydrogen through each membrane is therefore lower and the costs are increased.

- 15     The separation device 500 according to the above-described embodiments also has a number of advantages over a separation device with a tubular membrane instead of a planar membrane. The transportation distance of the hydrogen within the syngas is dependent on average spacing between adjacent membranes. With planar membranes,  
20     adjacent membranes are parallel to each other and so the average spacing between adjacent membranes is the minimum distance between the adjacent membranes. When tubular membranes are used, the membranes are not parallel to each other and the average spacing between adjacent membranes is greater than the minimum distance between adjacent membranes. The transportation distance of the hydrogen is therefore lower when planar  
25     membranes are used.

- In embodiments, hydrogen is collected in at least one outlet channel 501 and 504 between an edge of the substantially square part of each gas separation section 300 and the substantially annular part of each gas separation section 300. The outlet channel provides  
30     a flow path of hydrogen to an output port. Advantageously, the provision of a flow path for the hydrogen allows the membrane to have a regular shape, for example the membrane may be a solid square. This is advantageous over providing a hydrogen flow path that

requires making a hole in the plane of a membrane. In particular, this is advantageous over using annular membranes with a flow path for collected hydrogen through the middle of each annular membrane. Such an implementation would reduce the available membrane size. There would also be substantial pressure differences within the system.

5

Embodiments include a number of modifications and variations to the techniques as described above.

Embodiments have been described with reference to hydrogen being separated from the other constituents of syngas. Embodiments also include other applications. For example, hydrogen may be separated from other gas mixtures, such as hydrogen removal during the reaction of alkenes to alkynes and purification of hydrogen.

Embodiments include the use of other membranes than palladium membranes. The use of other membranes allows other gasses than hydrogen to be separated from a gas mixture. The separation device 500 according to embodiments can therefore be used to separate any of one or more gasses that can flow through the membranes from a gas mixture.

Embodiments have been described as a gas separation device 500. Embodiments may also be considered to be a gas cleaning device. That is to say, the separation device 500 according to embodiments can be used to increase the purity of hydrogen, or any other gas that can flow through the membranes 201.

As shown in Figure 4B, the mesh may be a plate that comprises a plurality of channels, with each of said plurality of channels being a second channel 204. The mesh has been described as steel mesh. Embodiments include the mesh being made of any other material that has the property of providing the required structural support. The mesh may have any structure that supports the substrates 203 that are attached to the mesh.

The membranes 201 have been described as having square-shaped planes. However, embodiments include the planes having other-shaped planes, such as circular planes or rectangular planes.



The hydrogen frames 301 and syngas frames 404 may comprise conduits. The flow paths of the hydrogen, syngas and/or retentate gas may be through these conduits in addition to, or instead of, the inlet/outlet channels 501, 502, 503 and 504.

5

Embodiments have been described with the separation device 500 comprising gas separation sections 300 with planar membranes. Although this is a preferred implementation of embodiments, embodiments also include the use of tubular membranes in the separation device 500. The membranes, substrate and mesh would have a  
10 tubular/cylindrical structure but otherwise may be substantially as described for the planar membranes according to embodiments.

The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather, the method steps  
15 may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without departing from the spirit and scope of the invention as set forth in the appended claims.

20

**Claims:**

1. A gas separation section for separating a first gas from one or more other gasses in a separation device, the gas separation section comprising:
  - 5 a first membrane that is substantially planar;
  - a second membrane that is substantially planar;
  - 10 a first substrate that has a first surface and a second surface, wherein the second surface of the first substrate is on an opposite side of the first substrate than the first surface of the first substrate;
  - a second substrate that has a first surface and a second surface, wherein the second  
15 surface of the second substrate is on an opposite side of the second substrate than the first surface of the second substrate; and
  - a mesh that is arranged between the second surface of the first substrate and the  
20 second surface of the second substrate;
  - wherein:
    - the first substrate and the second substrate are sintered plates;
    - 25 the first membrane is on the first surface of the first substrate;
    - the second membrane is on the first surface of the second substrate;
    - the first and second membranes are both permeable by at least a first gas and not  
30 permeable by one or more other gasses;

the thickness of the first membrane in a direction orthogonal to the plane of the first membrane is less than 10 micrometres; and

5 the thickness of the second membrane in a direction orthogonal to the plane of the second membrane is less than 10 micrometres.

2. The gas separation section according to claim 1, wherein the first gas is hydrogen and the one or more other gasses include carbon monoxide and/or carbon dioxide.

10 3. The gas separation section according to claim 1 or 2, wherein the first and second membranes comprise palladium;

and, optionally, the first and second membranes further comprise one or more other metals than palladium.

15

4. The gas separation section according to claim 3, wherein the first and/or second membrane comprises silver;

20 and, preferably, the membrane is between 15 wt% to 40 wt% silver with the rest of the membrane being palladium;

and, more preferably, the membrane is 77 wt% palladium and 23 wt% silver.

25 5. The gas separation section according to any preceding claim, wherein said thickness of the first and/or second membrane is between 0.2 and 4 micrometres, preferably between 1 and 3 micrometres.

6. The gas separation section according to any preceding claim, wherein the first and second membranes are substantially square shaped.

30

7. The gas separation section according to any preceding claim, wherein the mesh is a steel mesh.

8. The gas separation section according to any preceding claim, wherein:

the mesh is attached to the second surface of the first substrate at a plurality of locations between opposite edges of the second surface of the first substrate; and

5

the mesh is attached to the second surface of the second substrate at a plurality of locations between opposite edges of the second surface of the second substrate.

9. The gas separation section according to any preceding claim, wherein the mesh is

10

attached to both the first substrate and the second substrate such that the mesh attachments hold the second surface of the first substrate and the second surface of the second substrate substantially parallel to each other.

10. The gas separation section according to claim 9, wherein the second surface of the

15

first substrate is separated from the second surface of the second substrate by a distance in the range 2 mm to 30 mm.

11. The gas separation section according to any preceding claim, wherein:

20

the thickness of the first substrate is less than 3mm; and/or

the thickness of the second substrate is less than 3mm.

12. The gas separation section according to any preceding claim, wherein the gas

25

separation device further comprises:

a first gasket that is arranged to provide a gas seal at the edges of the first membrane; and

30

a second gasket that is arranged to provide a gas seal at the edges of the second membrane.

13. The gas separation section according to any preceding claim, wherein the mesh is

arranged in a channel that, in use, the first gas is arranged to flow through.

14. The gas separation section according to claim 13, wherein the gas separation device further comprises at least one frame that is arranged to provide a flow path of the first gas;
- 5 wherein the at least one frame is arranged to be in fluid communication with the channel such that, in use, the first gas flows from the channel into the flow path provided by the frame.
- 10 15. The gas separation section according to claim 14, wherein the frame comprises a substantially annular section that encircles the first and second membranes.
16. The gas separation section according to any of claims 12 to 15, wherein:
- 15 the first gasket is a single piece structure that comprises a substantially square section within a substantially annular section; and/or
- the second gasket is a single piece structure that comprises a substantially square section within a substantially annular section.
- 20 17. A separation device for separating a first gas from one or more other gasses, the separation device comprising:
- an inlet for receiving a gas mixture comprising a first gas and one or more other
- 25 gasses;
- a plurality of gas separation sections according to any preceding claim, wherein the plurality of gas separation sections are arranged in a stack;
- 30 a first outlet arranged to output the first gas that has passed through one or more of the membranes in the one or more gas separation sections; and

a second outlet arranged to output at least the one or more other gasses that have not passed through one or more of the membranes in the one or more gas separation sections.

- 5        18. The separation device according to claim 17, wherein the separation device further comprises an outer housing; and

the plurality of gas separation sections are arranged within the outer housing.

- 10       19. The separation device according to claim 18, wherein the outer housing is substantially cylindrical.

20. The separation device according to claim 18 or 19, wherein the first inlet is provided in an end section of the housing, such that, in use, the direction of flow of  
15       the gas mixture into the housing is substantially orthogonal to the planes of the membranes in the gas separation sections.

21. The separation device according to any of claims 18 to 20, wherein the housing further comprises an inlet that is arranged to receive steam for heating the gas  
20       separation sections.

22. The separation device according to any of claims 18 to 20, wherein the housing further comprises an inlet for purge gas that, in use, is supplied to one or more channels that the first gas is arranged to flow through after the first gas has passed  
25       through a membrane.

23. A method of separating a first gas from a gas mixture comprising the first gas and one or more other gasses, the method comprising:

- 30       feeding the gas mixture into a separation device according to any of claims 17 to 22;

receiving a first gas flow from the separation device that comprises substantially only the first gas; and

receiving a second gas flow from the separation device that comprises at least the one or more other gasses than the first gas.

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Fig. 1

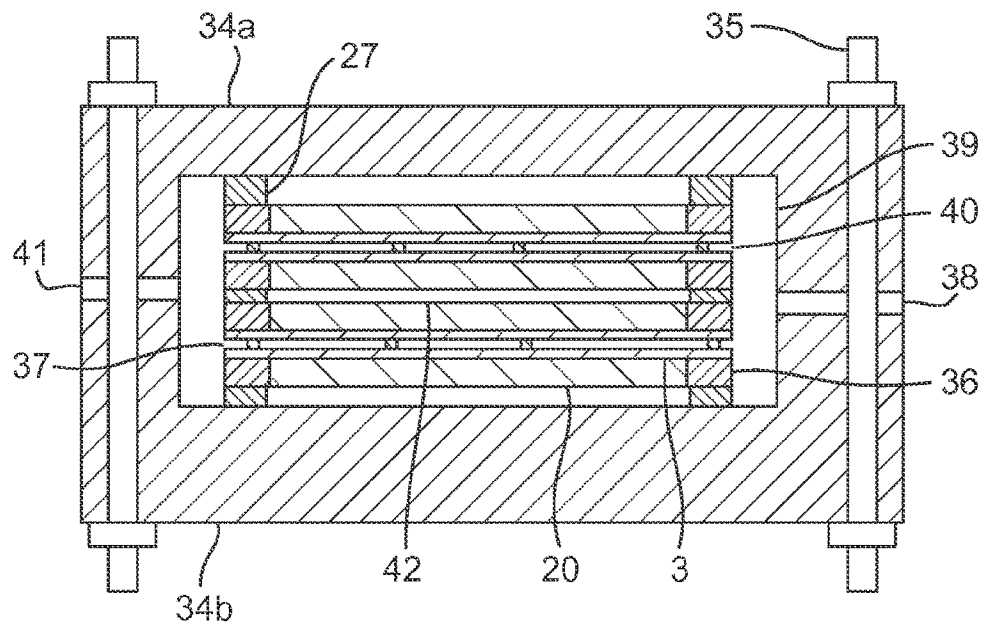
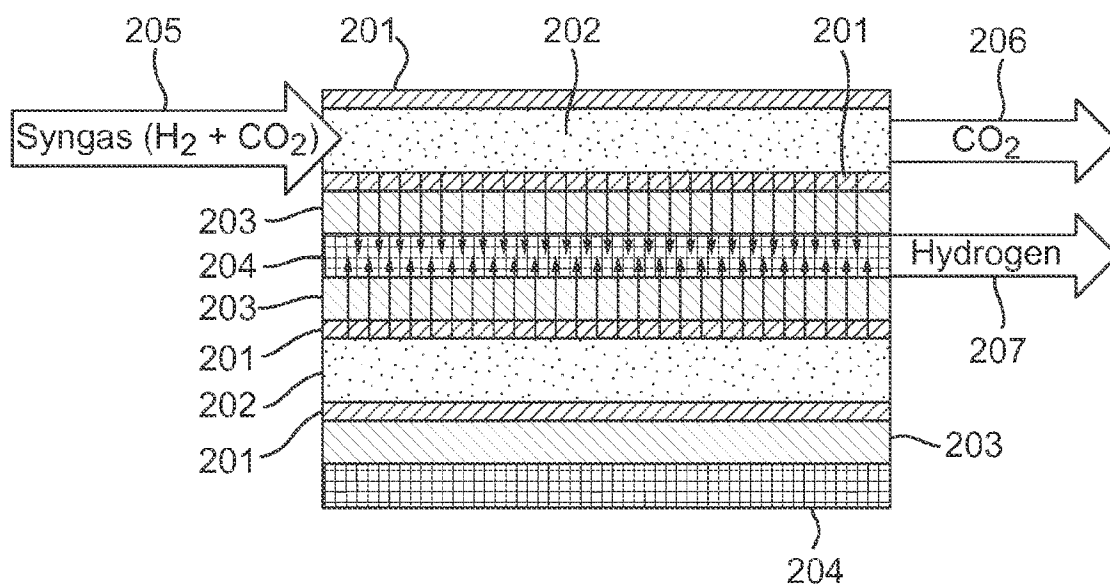


Fig. 2





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Fig. 3A

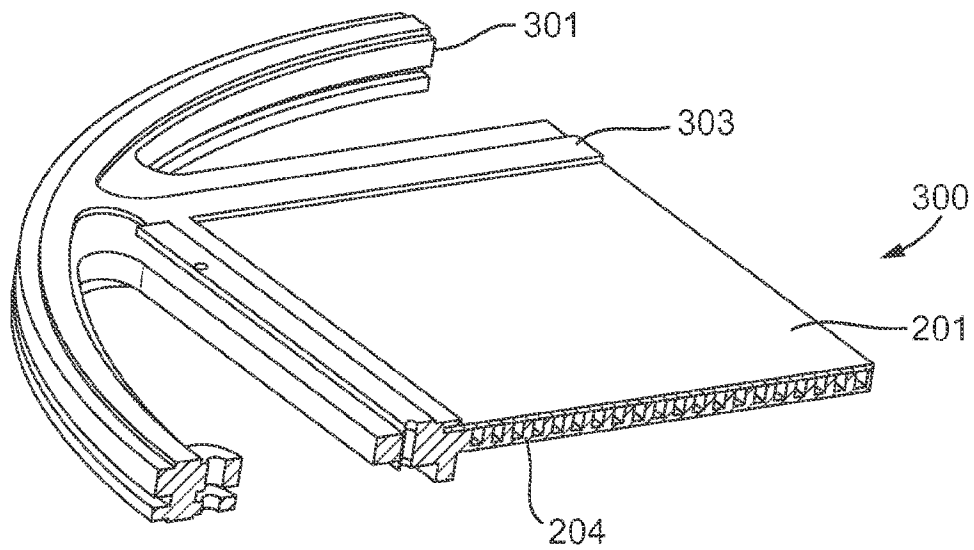
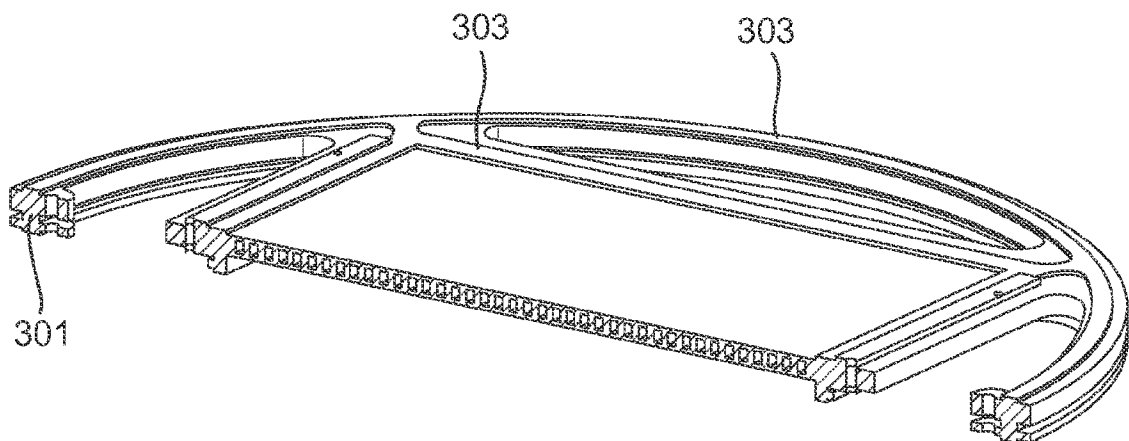
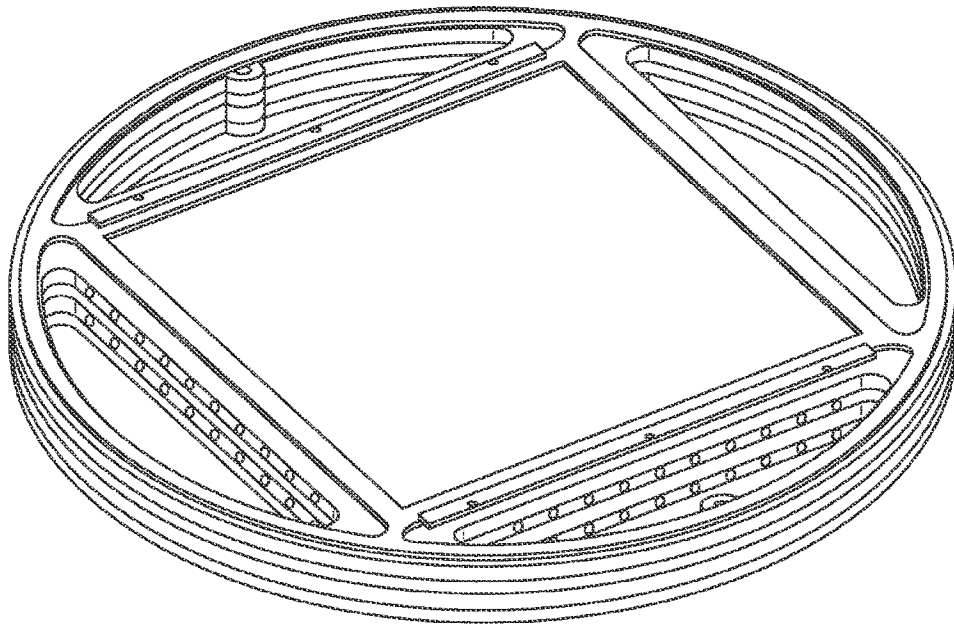


Fig. 3B



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Fig. 3C



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Fig. 4A

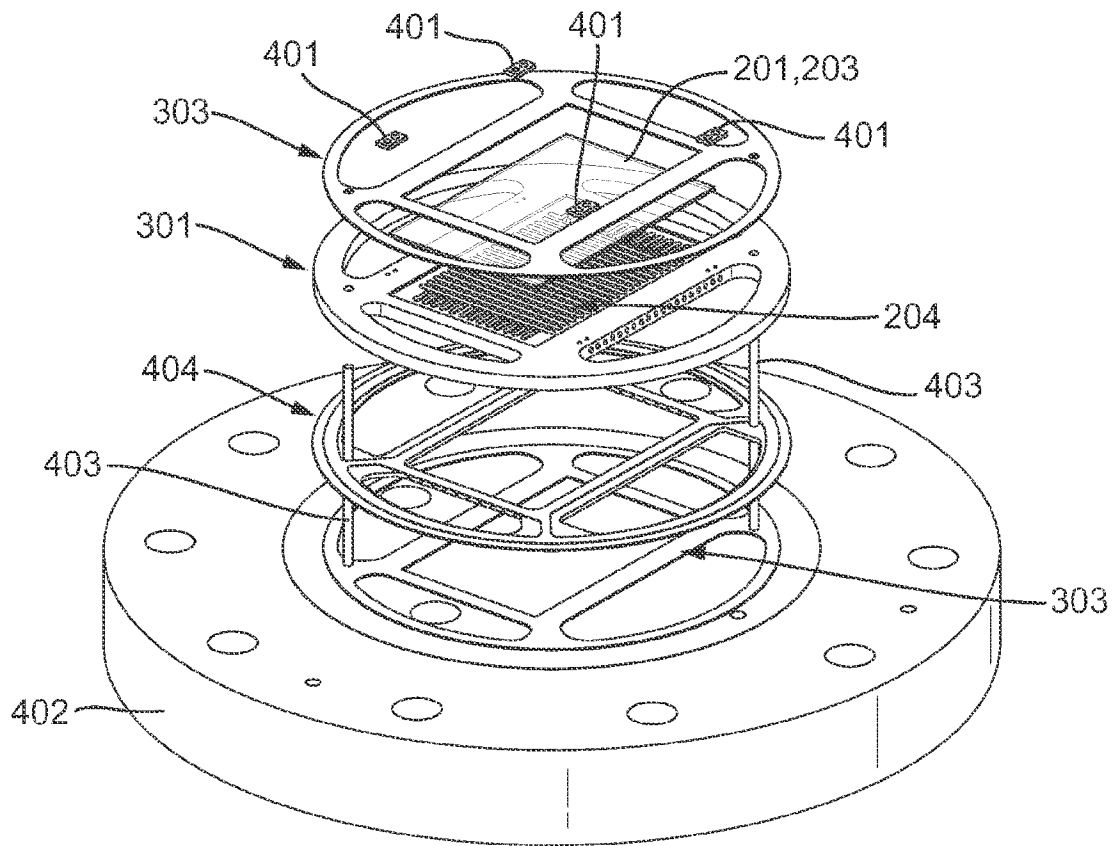
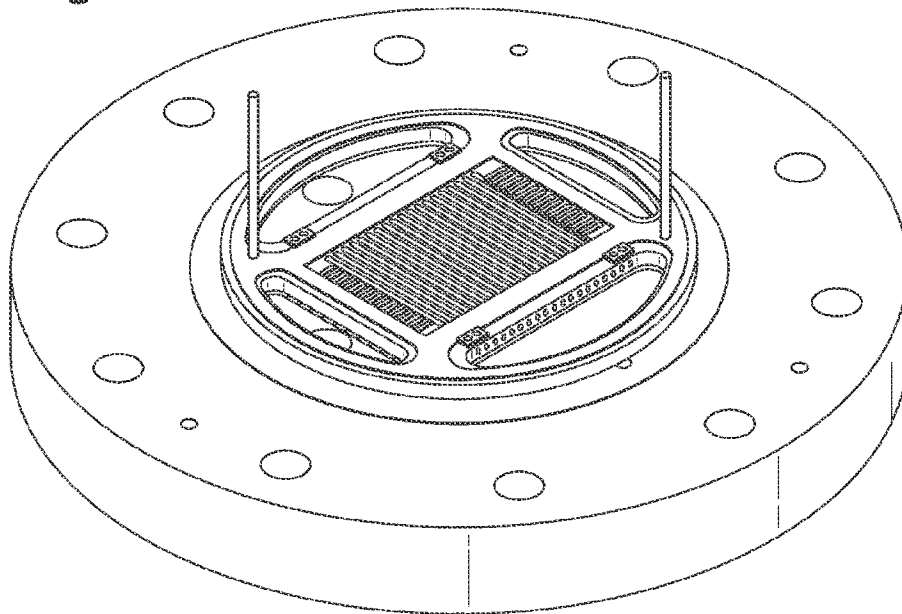
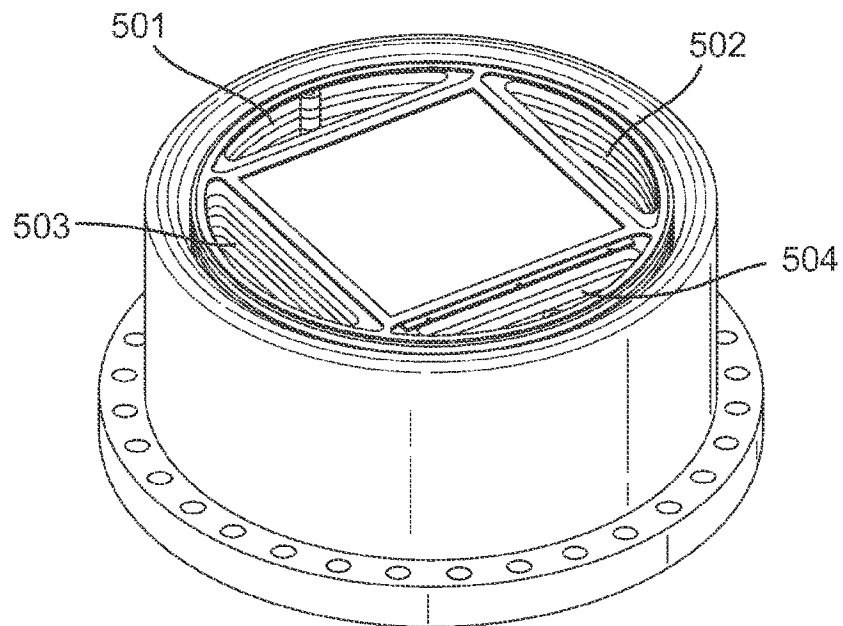


Fig. 4B



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Fig. 5



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Fig. 6A

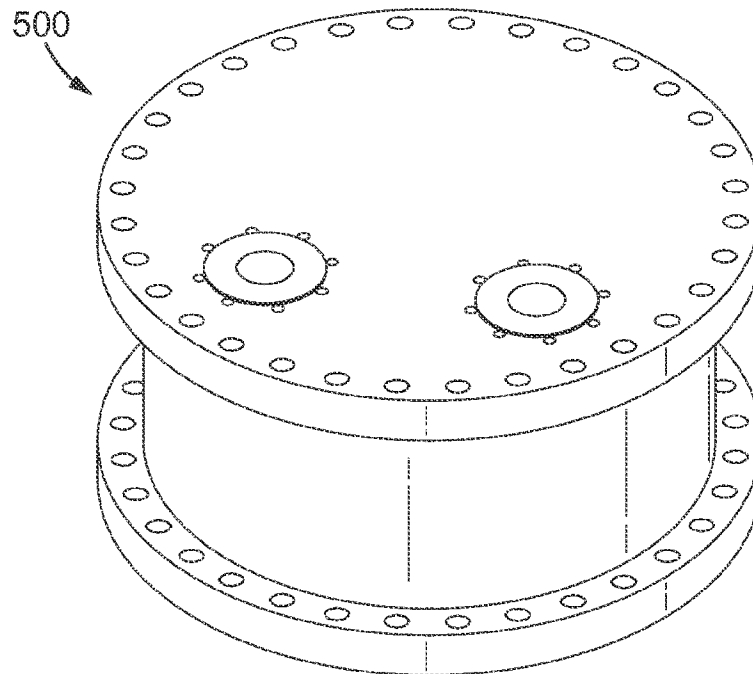
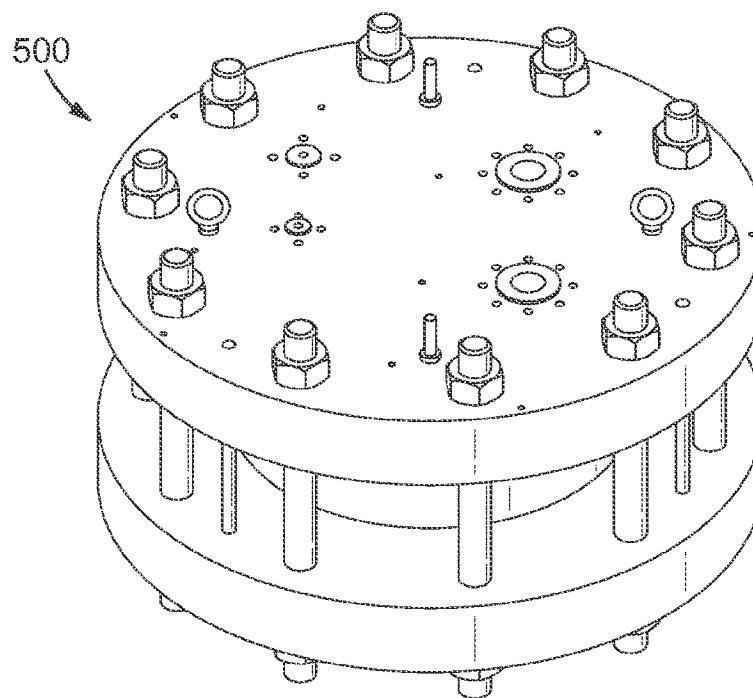


Fig. 6B



## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/068893

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/22 C01B3/02 B01D63/08 B01D67/00 B01D69/12  
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)

B01D C01C 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 practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y         | column 6, line 49 - column 7, line 26<br>column 8, line 6 - line 13<br>column 9, line 17 - column 10, line 31<br>column 11, line 24 - line 53<br>column 15, line 54 - column 16, line 49<br>column 13, line 46 - column 14, line 55;<br>figures 2-6 | 6,14-16                |
| Y         | US 6 494 937 B1 (EDLUND DAVID J [US] ET<br>AL) 17 December 2002 (2002-12-17)<br>column 18, line 54 - column 24, line 65;<br>figures 32-39                                                                                                           | 6,14-16                |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

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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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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/068893

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NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW,  
SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN,  
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**Published:**

- with international search report (Art. 21(3))
- with amended claims (Art. 19(1))

## HYDROGEN AND/OR AMMONIA PRODUCTION PROCESS

### FIELD

The present disclosure relates to hydrogen and ammonia production processes. Embodiments provide a system for generating syngas and then separating hydrogen  
5 from the syngas. The system according to embodiments may use the separated hydrogen to generate ammonia.

### BACKGROUND

It is generally believed that the greenhouse effect and the climate on Earth are  
10 closely linked to human-made emissions of carbon dioxide (CO<sub>2</sub>). These emissions are primarily formed by combustion of coal and hydrocarbons, i.e. by generation of heat, electric power as well as use in internal combustion engines. A desirable goal is to reduce the emission of CO<sub>2</sub> to the atmosphere. It is known art to reduce the emission of CO<sub>2</sub> from combustion of natural gas, e.g. by gas reforming and shift  
15 technology for preparation of a mixture consisting of hydrogen and carbon dioxide. These components are then separated, after which hydrogen may be used in a number of applications, such as electricity generation, heat generation and in different types of transportation. Hydrogen may also be mixed with natural gas to produce hytane, a fuel for domestic and industrial energy users. Carbon dioxide has  
20 industrial applications but may also be deposited after compression to a desired pressure. The deposition can be made on the bottom of the sea or in geological reservoirs, often called aquifers. The reservoirs can also contain hydrocarbons.

Hydrogen in the transport sector as fuel for fuel cells is gaining increased attention, and fueling stations for transportation vehicles are being deployed in several areas of  
25 the world, notably in the USA, Europe and Japan. Practically all of these fueling stations are based on hydrogen that is made by splitting water through electrolysis and compressed to typically 700 bar. Liquid hydrogen is being considered for heavier transport like ships and trains. Unfortunately, electrolysis has been calculated to be at least twice as costly as producing hydrogen by reforming natural gas. These  
30 calculations include costs of separation and liquefaction of coproduced CO<sub>2</sub> and payment of tariffs for deposition of CO<sub>2</sub> in underground reservoirs. Another

complicated issue with water electrolysis is calculation of the greenhouse effect, as most electricity is still produced from hydrocarbons with significant emission of CO<sub>2</sub> to the atmosphere. Therefore, producing hydrogen from natural gas with CO<sub>2</sub> storage is a significantly better option.

- 5 There is a general need to improve hydrogen production processes.

## SUMMARY OF INVENTION

According to a first aspect of the invention, there is provided a method of producing hydrogen, the method comprising: receiving a feed gas comprising hydrocarbons;  
10 performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide; performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide; performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate  
15 streams of hydrogen, carbon dioxide and a rest gas; and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the reforming process, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process; wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and  
20 more preferably at least 90%.

Preferably, the one or more reforming processes comprise an autothermal reforming process.

Preferably, the one or more reforming processes comprise a partial oxidation reforming process.

- 25 Preferably, the reforming process comprises a gas heated reforming process.

Preferably, the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

- 30 Preferably, the method further comprises: optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas;

and optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; wherein the pre-reforming process comprises: optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

Preferably, the hydrogen separation process comprises: inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane; outputting hydrogen from the permeate side of the Palladium membrane; and outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

Preferably, the hydrogen separation process comprises a PSA process.

Preferably, the rest gas that is recycled is fed back into the autothermal reforming process and/or another reforming process, such as a partial oxidation reforming process.

Preferably, the rest gas that is recycled is fed back into the water-gas-shift process.

Preferably, the rest gas that is recycled is fed back into the hydrogen separation process.

Preferably, the feed gas is natural gas.

Preferably, the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.

Preferably, the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

Preferably, the autothermal reforming process is supplied with oxygen from an air separation unit.

Preferably, the water-gas-shift process is conducted in one water-gas-shift reactor; wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C,

and/or at about 300 °C; and wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

Preferably, the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

- 5 Preferably, no additional steam is added between the reforming processes and the water-gas-shift process.

Preferably, the method further comprises operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

- 10 Preferably, water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

Preferably, water is not separated from the shifted gas before the hydrogen separation process.

- 15 Preferably, the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

Preferably, the carbon dioxide separation process is conducted cryogenically.

- 20 Preferably, the method further comprises generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

According to second aspect of the present invention, there is provided a hydrogen production plant arranged to perform the method of the first aspect.

According to third aspect of the present invention, there is provided an ammonia production plant arranged to perform the method of the first aspect.

25

## BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows a reforming process comprising a gas-heated reforming process and an autothermal reforming process.

Figure 2 shows a configuration of a hydrogen production process.

Figure 3 shows a configuration of a hydrogen production process according to an embodiment.

5 Figure 4 shows a configuration of a hydrogen production process according to an embodiment.

Figure 5 shows a configuration of a hydrogen production process according to an embodiment.

Figure 6 shows a configuration of a hydrogen production process according to an embodiment.

10 Figure 7 shows a configuration of a hydrogen production process according to an embodiment.

Figure 8 shows a configuration of a hydrogen production process according to an embodiment.

15 Figure 9 shows a configuration of a hydrogen production process according to an embodiment.

Figure 10 comprises Table 1.

Figure 11 comprises Table 2.

Figure 12 comprises Table 3.

Figure 13 comprises Table 4.

20 Figure 14 comprises Table 5.

Figure 15 comprises Table 6.

Figure 16 shows a configuration of an ammonia production process according to an embodiment.

## 25 DETAILED DESCRIPTION OF EMBODIMENTS

A known method for the production of a CO<sub>2</sub>-rich gas stream and a H<sub>2</sub>-rich gas stream comprises the following steps:

- a) natural gas and water are fed to a reforming reactor and are converted to synthesis gas, also referred to as syngas, under supply of an O<sub>2</sub>-containing gas. Syngas mainly comprises H<sub>2</sub> and CO;
- b) the gas stream from a) is shifted so as to produce a mixture of H<sub>2</sub> and CO<sub>2</sub> by reaction with H<sub>2</sub>O;
- c) CO<sub>2</sub> is separated from the gas stream from b) in a CO<sub>2</sub> separation unit;
- d) H<sub>2</sub> is separated from the CO<sub>2</sub>-depleted gas from c) in a H<sub>2</sub> separation unit.

The above method describes the basic principles behind the production hydrogen from natural gas with separation of hydrogen and CO<sub>2</sub>.

- Known techniques combust the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> as fuel. If a relatively high percentage of hydrogen has not been separated, then a significant amount of hydrogen will be wasted in this fuel. Furthermore, the combustion of any accompanying carbon containing species in the fuel produces uncaptured CO<sub>2</sub>.

- Most hydrogen producing processes from natural gas known in the art rely on the use of a steam reformer, and in some instances on an autothermal reformer (ATR), i.e. using an autothermal reactor, or a partial oxidation reactor (POX). However, use of a gas-heated-reformer (GHR) in combination with an autothermal reformer is considerably more energy efficient.

- Production and perspectives on syngas production has been described by J. R. Rostrup-Nielsen in *Catalysis Today*, volume 18, pages 305-324, 1993, and in volume 71, pages 243-247, 2002. There are several types of reformers for production of synthesis gas comprising steam reforming, autothermal reforming and partial oxidation. There are methods for producing synthesis gas by a combination of steam reforming and autothermal reforming. Combined reforming comprises steam reforming and autothermal reforming, normally in series. Gas heated reforming (GHR) utilizes hot gas, e.g. off-gas from autothermal reforming, to provide heat for reforming of a feed gas. GHR is described in a paper by K. J. Elkins et al. entitled "The ICI Gas-Heated Reformer (GHR) System" presented at the Nitrogen '91 International Conference, Copenhagen, June 1992.



Separation of CO<sub>2</sub> is frequently done by an amine washing process, a carbonate process, and sometimes by using a physical sorbent like methanol or ethers; or simply by washing with water.

5 Hydrogen may be separated from a hydrogen containing gas mixture by use of a pressure swing absorption/adsorption (PSA) processor. In some implementations of PSA processes by a PSA reactor, the PSA reactor is a large and costly part of the hydrogen plant. PSA processes may also result in CO<sub>2</sub> being released at low pressure, e.g. atmospheric pressure, and so there is a subsequent need for compression and cooling. Still, it can be feasible to use PSA for some hydrogen  
10 production plants.

Embodiments provide new and particularly advantageous implementations of systems for producing hydrogen from natural gas. Hydrogen production may be the main purpose of the system. However, embodiments also include using at least some of the hydrogen, or all the hydrogen, to produce ammonia. Ammonia is an  
15 alternative energy carrier to compressed or liquefied hydrogen. In addition to the production of fertilizers and some chemicals, ammonia may be used as fuel in energy, transportation, maritime and offshore markets.

Embodiments also provide a high carbon capture efficiency that may be at least 90% of the carbon in the feed gas, and preferably at least 97%.

20 Although embodiments may separate CO<sub>2</sub> by using an amine washing process, or other process, embodiments preferably use cryogenic separation to separate CO<sub>2</sub>. That is to say, the gas stream is cooled to a temperature, and at a pressure, where CO<sub>2</sub> is liquefied.

Cryogenic separation of CO<sub>2</sub> has in the known art been assumed to be  
25 disadvantageous as a smaller fraction of CO<sub>2</sub> is separated. However, embodiments avoid this disadvantage by providing novel process design. CO<sub>2</sub> is obtained directly in a liquid form, i.e. ready for transportation to a deposition site.

Embodiments advantageously re-use the remaining gas after separation of CO<sub>2</sub> and H<sub>2</sub> in the hydrogen production system. This improves the carbon capture efficiency  
30 of the system.

Embodiments include using a Palladium membrane (Pd-membrane) to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons. One advantage is that hydrogen is obtained with high purity; that may be greater than 99% and is often greater than 99.9%. Another  
5 advantage is that the gas containing CO<sub>2</sub> that does not pass through the membrane, which is referred to as the retentate, is at an elevated pressure, typically above 10 bar, more typically between 20 and 40 bar, but sometimes even at pressures up to 100 bar. It is even preferred that the Pd-membrane operates at an elevated temperature; 200-400 °C, or in a narrower range above or around 300 °C, so that it is  
10 well suited for operation down-stream of the water-gas-shift (WGS) reactor or reactors.

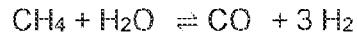
Embodiments also include using a PSA process, or PSA processes, to separate hydrogen from the reformed natural gas; or more generally from a reformed gas containing hydrocarbons.

15 Embodiments include receiving a supply of natural gas, or more generally a hydrocarbon containing gas from any source. The natural gas may be cleaned and pre-treated in a suitable manner so that the gas feed mainly comprises methane after treatment. Such cleaning typically comprises sulfur removal, for example by one or more ZnO absorbers. Sometimes heavy metals, typically Hg, are also removed. The  
20 pre-treatment may also comprise a pre-reforming process whereby higher hydrocarbons, such as ethane, are converted by steam to methane and CO<sub>2</sub>.

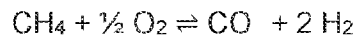
The reforming process according to embodiments may take place at a pressure within the interval 10 to 200 bar.

The water-gas shift reaction according to embodiments may take place in one or  
25 more shift reactors. Steam may be supplied to the shift reactor, but the shift reactor may also be operated without supply of steam as steam already may have been introduced into the reformer. At the outlet of the shift reactor, the carbon content may comprise CO<sub>2</sub> and methane. CO<sub>2</sub> may be about 2% to about 5% by volume or higher. Methane may be about 2% to about 5% by volume or higher.

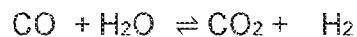
30 The following chemical reactions may take place during production of synthesis gas and hydrogen by reforming of natural gas:



1. Steam reforming



2. Partial oxidation



3. Shift reaction

The heat of reaction for the strongly endothermic steam reforming can be provided either by external heating, as in a steam reformer, or by partial oxidation in an autothermal reformer.

In a steam reformer (SR) natural gas (i.e. methane) is converted in a tube reactor at high temperature and relatively low pressure. A steam reformer consists of many reactor tubes, e.g. 200-250 tubes with typical lengths of 12-13 meters, inside diameter of about 10 cm and an outside diameter of about 12 cm. This is a space demanding unit with a length of 30-50 meters, width of 10-12 meters and a height of 15-20 meters. Conventional steam reformers are operated in the pressure range from 15 to 30 bar. The outlet temperature of the gas from a conventional steam reformer is approximately 950 °C. The energy which is used to carry out the endothermic reactions is supplied by external firing/heating (top-, side-, bottom- or terrace-fired). The ratio between steam and carbon is from 2.5 to 3.5, and the ratio between hydrogen and carbon monoxide in the produced stream is from 2.7 to 3.0. Synthesis gas produced from a steam reformer may contain approximately 3% methane by volume.

Alternatively, the reforming of natural gas (equation 1 and 2 above) can take place in an autothermal reformer (ATR). In an ATR, natural gas (methane) is fed together with oxygen or air into a combustion chamber. The energy which is required to operate the endothermic steam reforming reactions is provided by the exothermic reactions between hydrocarbons and/or hydrogen and oxygen. The temperature in the combustion chamber can reach more than 2000 °C. After the combustion chamber the reactions may be driven to equilibrium over a catalyst bed before the synthesis gas leaves the reactor at approximately 1000-1050 °C. The size of such a unit could be a height of 10-15 meters and a diameter of 5-6 meters. A typical ratio of steam:carbon in the output gas is from 0.6 to 1.4. The ratio of hydrogen to carbon monoxide in the output gas is lower than 2. Typical methane slip, i.e. amount of

unconverted methane, is 1-2% by volume in the product stream. The ATR can be operated at higher pressure than the SR.

A further option for reforming natural gas is a partial oxidation reactor (POX) which also is an autothermal reformer except that the unit does not comprise a catalyst bed.

- 5 The exit temperature for a POX is higher than for a typical ATR, sometimes significantly higher and it may be above 1200 °C. POX is often characterized by no steam added to the feed. A catalyst might be included, thus defining a catalytic partial oxidation (CPOX) reactor.

- 10 Reforming of natural gas can also be made by combined reforming (CR) which is a combination of a steam reformer (SR) and an autothermal reformer (ATR). A combination of SR and ATR makes it possible to adjust the composition out of the reformer unit by regulating the efforts on the two reformers. In combined reforming, SR is operated at milder conditions (i.e. lower outlet temperature), which leads to a high methane slip. The residual methane is then reacted in the ATR. The ratio of  
15 steam:carbon is in the area 1.8-2.4, with a ratio of hydrogen to carbon monoxide in the product gas higher than 2.

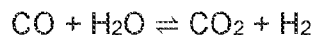
- From the above, it is clear that the conventional reformer unit has a very large footprint (SR), and that the exit gas is at a high temperature, typically 950-1100 °C. Conventionally, the exit gas is cooled down rapidly using a waste-heat-boiler (WHB)  
20 that produces steam. Rapid cooling and using tubes with boiling water are important to be able to control material corrosion by metal dusting. It has been found, however, that a more efficient process is experienced if the hot output gas is used to reform part of the natural gas before it enters the autothermal reformer. This combination of ATR with oxygen and a gas-heated-reformer (GHR) has been tested in a  
25 demonstration unit for production of methanol. This development originates in ICI in the 1980s to completely remove the traditional steam reformer in their Leading Concept Methanol (LCM) process.

- Figure 1 shows an efficient reforming process that may be used in embodiments. The hot exit gas from the reformer is used to reform part of the natural gas before it  
30 enters the autothermal reformer. Instead of burning fuel gas to provide the heat for the reforming reactions, the hot, autothermally reformed gas 22 is used to heat the

catalyst tubes in a GHR 1. The feed gas 11 first passes through the catalyst in the GHR 1, then the partially reformed gas in stream 21 passes through the ATR 2, and finally the reformed gas in stream 22 passes through the heating side of the GHR 1 to provide the heat for the initial reaction. Thereby the exit temperature of the syngas 12 is reduced significantly to the range 500-600 °C and needs only moderate further cooling before the water-gas-shift process (WGS).

Although embodiments include the reforming process shown in Figure 1, embodiments also include alternatively using any other type of reforming process. For example, embodiments include only using an autothermal reformer or only using a gas-heated-reformer.

After reforming of the natural gas and cooling, the gas mixture is shifted. The gas mixture from the reformer reactor contains mainly the gas components CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and some CH<sub>4</sub>. Between these components there is an equilibrium relation given by the stoichiometric equation:



This reaction is called the water-gas-shift (WGS) reaction, and by operating a shift reactor at certain conditions the equilibrium can be forced to the right and a gas mixture is obtained which is rich in hydrogen and carbon dioxide, and where the concentration of carbon monoxide is low. Sufficient reaction velocity is provided by use of suitable catalysts, and in processes where a high degree of reaction of CO is desirable (e.g. ammonia synthesis) two fixed bed reactors may be used in series, a high temperature shift reactor and a low temperature shift reactor, respectively. Two steps are chosen because the equilibrium is favored by low temperature, whereas the reaction velocity is favored by high temperature. By selecting two reactors working in series, a smaller total reactor volume is achieved. The process is nearly pressure independent and normally the same pressure as in the reformer is used. Typical temperature out of the first reactor is 420 °C. and out of the second reactor 230 °C. The catalyst in the first step may be based on chromium/iron, whereas the catalyst in the second step may be a copper/zinc catalyst. In the shift unit CO and H<sub>2</sub>O are reacted to form CO<sub>2</sub> and H<sub>2</sub>, and in known techniques it is often a

requirement that the mentioned reaction is driven to the right to the highest possible degree, so that as little CO as possible is present in the gas mixture exiting the shift unit. A low content of CO in the mentioned gas mixture again may give a high purity of the H<sub>2</sub>-rich gas stream out of the separation unit.

- 5 In known techniques the shift reactor is operated so that the ratio H<sub>2</sub>O:CO to the shift reactor is high, e.g. equal to 10:1, so that there is a high conversion of CO.

Embodiments may differ from such techniques by optimizing the processes in a WGS reactor in conjunction with a hydrogen separation processes by a Palladium membrane. The efficiency of a Pd membrane may be improved by operating at a  
10 certain elevated temperature. Preferably, only a high- or medium- temperature WGS is therefore applied before the membrane. A low-temperature WGS may also be used after the membrane and the shifted gas partly recycled, i.e. fed back into one of the earlier processes in the hydrogen production process.

In a preferred embodiment, the temperature of the WGS process is determined in  
15 dependence on an operating condition of the Pd-membrane. For example, the temperature of the WGS process may be set substantially at the operating condition of the Pd-membrane, e.g. about 300 °C, thereby avoiding any need for heat exchange between the two units. It is not necessary for the WGS process to be operated in a way that maximizes the conversion of CO because the rest gas is  
20 recycled back into the earlier processes. Embodiments include no additional steam being added before the WGS reactor. When the Pd-membrane is operated at about 300 °C, a Cu-based catalyst may be used.

If a different to Pd-membrane hydrogen separation process is used, like PSA, it still might be feasible to operate only one WGS reactor, e.g., an isothermal shift reactor.  
25 Ultra-high conversion of CO is not always needed, and can be rectified by recycle of rest gas.

Gases in the mixture after the shift reactor, or the shift reactors, can be separated more or less completely based on the different properties of the gas molecules. The most common techniques are absorption, adsorption and cryogenic distillation.  
30 CO<sub>2</sub> is an acid gas, and the most widely used method to separate the mentioned gas

from other non-acid gas molecules is absorption. During absorption the different chemical properties of the gas molecules are utilized. By contacting the gas mixture with a basic liquid, the acid gases will to a high degree be dissolved in the liquid. The liquid is separated from the gas and the absorbed gas can then be set free either by  
5 altering the composition of the liquid or by altering pressure and/or temperature. For separation of CO<sub>2</sub>, aqueous solutions of alcoholamines can be used. The absorption takes place at a relatively low temperature and a high pressure, while stripping of the gas from the liquid is carried out at a relatively high temperature and low pressure. To liberate CO<sub>2</sub> from the amine phase in the stripping unit, stripping steam is usually  
10 used. If the partial pressure of CO<sub>2</sub> in the gas into the absorber is high, e.g. higher than 15 bar, it is possible to obtain high concentrations in the amine phase, and a large part of absorbed CO<sub>2</sub> can be set free in the stripping unit at elevated pressure, e.g. 5-8 bar. Other absorption technologies rely on alternative physical liquid absorbents like methanol at reduced temperature.

15 Embodiments preferably separate hydrogen from the gas output from the WGS reactor using a membrane. In particular, a Pd-film membrane may be used. By the use of one or more semipermeable or dense membrane units, molecules of different size and different properties can be made to permeate the membrane at different velocities. This principle can be utilized to separate gases. For the gas mixture from  
20 the WGS reactor, membranes can be selected where H<sub>2</sub> permeates rapidly, whereas CO<sub>2</sub> permeates slowly or not at all, so that separation of the different gas components is achieved. The membrane may be a Palladium membrane.

The driving force over the membrane is the difference in partial pressure, i.e. of hydrogen between the process gas (which is the received gas on the retentate side  
25 of the membrane) and gas on the permeate side of the membrane. As hydrogen in many cases is required at an elevated pressure, a way to secure partial pressure difference is to use a sweep gas of steam at the permeate side and then condense out water afterwards, leaving hydrogen at a pressure comparable to the process gas. Although embodiments include using a sweep gas, this is optional and embodiments  
30 also include not using a sweep gas.

Embodiments may alternatively use a combination of solid membranes and liquid membranes through which there is a rapid permeation of CO<sub>2</sub>, while H<sub>2</sub> is kept back.

Embodiments may alternatively use PSA to separate hydrogen from the gas output from the WGS reactor. PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and  
5 differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material. In the present mixture of gases, CO, CO<sub>2</sub> and CH<sub>4</sub> are adsorbed, letting the hydrogen pass through  
10 at process pressure. Not to overload the adsorbent, water is condensed before the PSA unit. Alternatively, the temperature can swing instead of the pressure.

Capturing CO<sub>2</sub> by refrigeration is a cost and energy efficient method compared to other technologies. In known techniques, electricity may be used to drive the compressors. The main challenge has been that only in the order of 90% of CO<sub>2</sub> is  
15 captured this way, or perhaps 93% by optimizing conditions. In addition, there are some carbon losses from unconverted CO and CH<sub>4</sub> and these reduce the overall carbon capture to 90% or below. Specific advantages of using cryogenic CO<sub>2</sub> separation are that the product is directly in the liquid form needed for deposition and no additional compression is required.

20 Embodiments include separating out CO<sub>2</sub> and then depositing the separated CO<sub>2</sub>. Large amounts of CO<sub>2</sub> can be deposited according to various methods, such as deposition in very deep oceans, deposition in deep water geological reservoirs and deposition in oil reservoirs wherein the gas at the same time functions as drive agent for enhanced oil recovery. The two last mentioned storage methods are operated  
25 commercially. In these storage forms the CO<sub>2</sub> gas has to be brought to high pressure and in liquid form for transport in pipelines to a deposition well and further to injection. The injection pressure will vary, but could be in the range 50 to 300 bar. If the CO<sub>2</sub> gas can be separated from the H<sub>2</sub>/CO<sub>2</sub> mixture at an elevated pressure, significant compression work can be avoided.

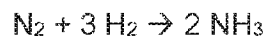
30 Embodiments may allow a selection to be made between collecting hydrogen and CO<sub>2</sub> at the high (process) pressure. A hydrogen pressure requirement varies with application, but high pressure or liquid hydrogen, is needed for storage and in



transportation applications. As it is more demanding to pressurize hydrogen than CO<sub>2</sub>, separation technologies that provide hydrogen at high pressure are sometimes preferred. This benefit can, however, be outweighed by the efficiency of a hydrogen-permeable membrane.

- 5 Embodiments include using an air separation unit (ASU) to generate oxygen. The oxygen may be supplied to an autothermal reactor, ATR, or a partial oxidation reactor (POX), used in the reforming process. The ASU may cryogenically separate air into oxygen and a gas mixture that mostly comprises nitrogen. Embodiments include using the nitrogen, from the ASU, and hydrogen, from the membrane separator, to  
10 generate ammonia.

Combining nitrogen with hydrogen allows production of ammonia, NH<sub>3</sub>, according to the reaction:



- Ammonia can be used as an environmentally friendly fuel as long as any CO<sub>2</sub>  
15 generated during production is captured. The benefits of using ammonia include ease of transportation and handling. Liquid ammonia can be stored in vessels at about 17 bar.

The ammonia process is favored by high pressures, and an elevated temperature is needed for sufficient reaction rate.

- 20 A known production technique of ammonia is from natural gas, or sometimes from higher hydrocarbons, by reforming the gas to syngas that is shifted to mostly hydrogen and CO<sub>2</sub>. Using air in the process stream, like applying an ASU, gives a mixture of hydrogen, nitrogen, water and CO<sub>2</sub> after shift conversion. The shift reaction is frequently carried out in two steps, high-temperature and low-temperature  
25 shift, to convert CO to low levels. Before the ammonia synthesis, water is knocked out and CO<sub>2</sub> removed by elaborate means. Further, residual CO and CO<sub>2</sub> has to be removed as they are poisons for the catalyst, and this is done by methanation;





The ammonia synthesis loop is also known as Haber-Bosch synthesis. The reaction is run over a catalyst that typically is promoted magnetite. Single pass conversion over the catalyst is around or below 20% and, therefore, significant recycle is required. The pressure is in the range 60-200 bar depending on process design. This is significantly higher than reforming and shifting natural gas that takes place in the pressure range 20-35 bar. On the other hand, the reaction pressure to make ammonia is significantly lower than the 300-700 bar required for hydrogen as energy carrier. Reaction temperature is ca. 450 °C. There have been many types of design of ammonia plants during the last 60 years. One option that has been explored is to produce hydrogen from steam reforming combined with PSA, and combined this hydrogen with nitrogen from an ASU-unit. Such a plant, however, is not favorably designed for separating a pure CO<sub>2</sub>-stream for storage.

Embodiments are described in more detail by the following examples of embodiments and figures.

Process simulations using the program UniSim are based on natural gas with molar composition 88.8% methane, 5.6% ethane, 2.0% propane, 1.6% higher hydrocarbons, 1.5% CO<sub>2</sub> and 0.6% nitrogen. The gas is delivered at 48 barg and 400 °C, and after sulfur removal. The natural gas flow is 4625 kg/h; 246 kmol/h. Hydrogen specification is > 99.97 mol% for fuel cells, and specification for CO<sub>2</sub> is dry at > 95 mol%. Oxygen is supplied at 40 barg and 20 °C.

A number of process schemes are analyzed. These include one comparative example and a number of implementations of embodiments, four of which are summarized in Table 1 in Figure 10. The schemes vary in WGS temperature, use of Pd-membrane or PSA for hydrogen separation, use of amine solvents or cryogenic CO<sub>2</sub> separation, as well as the position of water condensation.

The membrane may be always operated at a preferable temperature for permeation of hydrogen through the membrane. For example, the membrane may be operated at 300 °C. However, the WGS may be operated at 256 °C for highest CO conversion,

but at 300 °C when the shifted gas is directly introduced to the membrane; i.e. without any heat exchange and water condensation.

The conditions of Embodiment Example 2 are applied in Embodiment Examples 5-7, where recycle of rest gas is used.

- 5 The following reasonable assumptions are made, but without fixing these conditions: in amine cases, it is assumed that 100% of inlet CO<sub>2</sub> is removed by the unit; in membrane cases, 93% H<sub>2</sub> separation is assumed; produced H<sub>2</sub> from the membrane unit is at 3 bar and compressed to 350 bar for export; the final CO<sub>2</sub> stream is delivered at -26.2 °C at 16 bar. It is understood that the applied conditions are
- 10 reasonable for comparing different process schemes, but that a variety of other conditions can be used; e.g. for different natural gas compositions, requirements for delivery of hydrogen and CO<sub>2</sub>, and site specific conditions like possibilities for integration with other process units and the availability of electricity from the grid.

### Comparative Example

- 15 Figure 2 is a process flow sheet showing production of hydrogen and CO<sub>2</sub> by combination of ATR 2 and GHR 1 according to a comparative example to embodiments.

The natural gas 31 is pretreated in unit 3 that comprises sulfur removal followed by saturation with water. A small portion of the hydrogen stream 101 is optionally added to the pretreated natural gas 41 as stream 103 and fed to the optional pre-reformer 4.

20 The syngas production, by the ATR 2 and GHR 1, is as described in Figure 1 with units with corresponding reference signs. The heat recycle 22 is the exit gas from the ATR used to heat the GHR. Oxygen 51 from an air separation unit (ASU) 5 is added to the ATR 2. The ASU separates cryogenically air 53 into oxygen 51 and nitrogen 52, sometimes also producing noble gases like argon. It should be

25 understood that embodiments include any other means for producing oxygen, or air enriched in oxygen, such as by using vacuum or pressure swing adsorption, or by using a membrane.

- The produced syngas 12 is shifted to increase the content of hydrogen and CO<sub>2</sub> in one or more shift reactors 6, i.e. water-gas-shift reactor(s) 6, to produce the shifted
- 30

gas 61. Steam may be added to the gas mixture before the gas mixture is input into the shift reactor(s) 6. The addition of steam increases the efficiency of the shift reaction. The shifted gas 61 is subsequently cooled in the condenser 7 to remove its water content 72, thus obtaining dry shifted syngas 71. Amine type separation process 8 separates CO<sub>2</sub> 81 from the shifted gas, and the CO<sub>2</sub> 81 is then compressed 9 and liquefied. The produced CO<sub>2</sub> 91 may be stored at site, shipped for permanent storage or directly injected into a geological formation for storage. Hydrogen 101 is separated in the process 10 by the known technique of pressure-swing absorption/adsorption (PSA), that separates the hydrogen from the gas 82 that has already been depleted of CO<sub>2</sub> by the process 8. The separate outputs from the process 10 are hydrogen 101 and a rest gas 102. The rest gas 102 contains remnants of CO and CH<sub>4</sub> together with unseparated CO<sub>2</sub> and hydrogen. The energy in the rest gas is utilized for fuel in fired heater(s) for preheating of feed gases natural gas and water/steam. Finally, the produced hydrogen 101 is compressed 11 to give hydrogen 111 at 340 bar.

The simulations show that production of 100 kNm<sup>3</sup>/hr hydrogen requires 35.7 kNm<sup>3</sup>/hr of NG and 16.7 kNm<sup>3</sup>/hr of oxygen. 622 tons of CO<sub>2</sub> is captured each year, assuming that the PSA rest gas 102 is used for combustion and the exhaust gas CO<sub>2</sub> emitted to the atmosphere. This gives a CO<sub>2</sub> capture efficiency of 95.4%. Electric power demand at 18.5 MW for compressors is delivered as renewable energy. Energy efficiency from natural gas to hydrogen is 80.4% based on lower heating values.

### Embodiment example 1

Figure 3 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 1. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

The present embodiment differs from the above-provided comparative example in that hydrogen separation is performed before CO<sub>2</sub> separation. After the WGS

process, the shifted gas enters a hydrogen separation vessel that comprises a Pd-membrane 12. The hydrogen separation vessel may receive the output gas from the WGS reactor on the retentate side of the Pd-membrane. Hydrogen passes through the Pd-membrane to reach a permeate side of the Pd-membrane. The hydrogen on the permeate side of the Pd-membrane is output as stream 121. The gas stream output from the retentate side of the Pd-membrane is hydrogen-depleted gas 122.

The hydrogen stream 121 is sent to compressor 11 while the hydrogen-depleted gas stream 122 is depleted of water 72 in the condenser 7. The dried gas 73 is then input into the amine separator 8 that outputs CO<sub>2</sub> stream 81 and a rest gas 83.

CO<sub>2</sub> stream 81 is compressed 9, and the CO<sub>2</sub> depleted rest gas 83 may be used for providing energy in fired heater(s).

Advantageously, the use of a Pd-membrane separator for separating hydrogen as the subsequent process to the WGS process allows the hydrogen separation process to be performed particularly efficiently and effectively. In particular, the temperature and/or pressure conditions in the WGS reactor may be selected in order to substantially optimize the operating conditions of the membrane separator (e.g. to maximize the separation of hydrogen in the membrane separator).

### **Embodiment example 2**

Figure 4 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 2. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane and water condensation 7 may be as described with reference to Figure 3 with corresponding reference signs.

A difference between embodiment example 2 and embodiment example 1 is that the amine unit 8 of embodiment example 1 is replaced with cryogenic separation 13 of CO<sub>2</sub> 131 from the dried gas 73, giving the rest gas 132 for use in fired heater(s).

### **Embodiment example 3**

Figure 5 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 3. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with  
5 corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. This embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as  
10 stream 71. In addition, reducing the water concentration before the membrane unit may advantageously increase the hydrogen concentration and may protect materials in the membrane unit.

The use of water condenser 7 on the gas output from the retentate side of the membrane separator 12 is optional.

15 CO<sub>2</sub> 81 is removed in an amine unit 8 leaving an energy rich rest gas 84.

#### **Embodiment example 4**

Figure 6 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment example 4. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming  
20 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs.

The present embodiment contains two condensers 7 for depleting water, streams 72 and 74, respectively, placed before and after the Pd-membrane 12. Such a  
25 configuration allows the shifted gas 61 to be heated to the ideal temperature before entering the membrane unit as stream 71.

CO<sub>2</sub> 131 is removed in the cryogenic unit 13 leaving an energy rich rest gas 132.

A comparison of the comparative example and embodiment examples 1-4 is provided below.

A comparison of performance of the comparative example and embodiment examples 1, 2, 3 and 4 is listed in Table 2 in Figure 11. There are, in addition, differences in investment and operating costs (i.e. CAPEX and OPEX). As to the investment costs, prices from vendors show that for hydrogen separation, PSA is considerably more costly than using a Pd-membrane, and that for CO<sub>2</sub> separation, using amine is significantly more costly than cryogenic separation. In addition, the footprints of PSA and amine are much larger than for Pd-membrane and cryogenic CO<sub>2</sub> separation.

Using a Pd-membrane, as in embodiment examples 1-4, is advantageous due to lower cost, smaller footprint and a higher hydrogen recovery factor than the comparative example. Note from the H<sub>2</sub> recovery factor that only 7% of the hydrogen in the shifted gas is lost in embodiment examples 1-4, compared to 14% in the comparative example. The percentage of carbon captured is above the 95% mark for embodiment examples 1 and 3, which is fully acceptable for most projects, although these still use amine separation of CO<sub>2</sub>. The amine separation in these two embodiment examples is, however, significantly simpler than in the comparative example, due to the more than 3-fold higher concentration of CO<sub>2</sub> in the inlet gas. Other factors to be considered are the conversion in the WGS (see Table 2 in Figure 11), and differences in how water is condensed (see Table 1 in Figure 10 as well as the figures).

Known techniques are based on the assumption that a high conversion of CO in the WGS reactor results in better system performance with regard to hydrogen and CO<sub>2</sub> recovery. However, test of embodiment examples show that the performance of the separation technologies is more dominant on the overall system performance. Accordingly, operating the WGS at 300 °C is advantageous.

There is no condensation of water and heat exchange after WGS and before the Pd-membrane in Embodiment Examples 1 and 2, in contrast to Embodiment Examples 3 and 4. The discussed advantages are summarized in Table 3 in Figure 12. It follows that using a Pd-membrane is preferable compared the comparative example, and that there is no need to adjust temperature and knock out water directly after WGS.

#### **Embodiment examples 5-7**

Figure 7 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to embodiment Examples 5-7.

The processes in embodiment Examples 5-7 may be substantially the same, or identical, to Embodiment Example 2 except that the rest gas 132 is recycled to the ATR 2.

The oxygen feed 51 may be adjusted to secure a constant exit temperature from ATR of about 1020 °C. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. The separation of hydrogen by a Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation 13 may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest gas 132 is used as recycle-gas to the ATR 2. The processes in the ATR 2 are therefore adapted so that the rest gas can additionally be received by the ATR 2.

The difference between Embodiment Examples 5-7 is in the amount of rest gas that is recycled, which is detailed in Table 4 in Figure 13.

#### **Comparison of Embodiment Examples 2 and 5-7**

In Table 4 in Figure 13, Embodiment Examples 5-7, with recycle of rest gas, are compared to Embodiment Example 2. Although Embodiment Example 2 shows good performance, as seen in Table 3 in Figure 12, it is desirable to improve the efficiency of CO<sub>2</sub> capture and the carbon capture fraction. Embodiments achieve this by recycling at least part of the rest gas to the reformer section. The results outlined in Table 4, in Figure 13, show a surprising effect in that much better performances are reached. Hydrogen production increases, with a recovery of 99% for Embodiment Example 7 (90% recycle), compared to 93% H<sub>2</sub> recovery for Embodiment Example 2 as defined in Table 2 in Figure 11; hydrogen loss is reduced from 7% to 1%. Simultaneously, the carbon capture increases from 90% in Embodiment Example 2 to 99% in Embodiment Example 7, the best performance of all examples.



When the production and separation efficiencies increase, more oxygen is needed in the ATR and less fuel gas is available for heat generation. The advantages summarized in Table 5, in Figure 14, indicates that a high degree of recycle is preferable. Probably more important is that a superior carbon capture fraction, as in  
5 Embodiment Example 7, is considered a decisive advantage in many hydrogen projects.

### Embodiment Example 8

Figure 8 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 8 which may be identical to Embodiment  
10 Example 2 except that the rest gas 133 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the WGS 6. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as  
15 described in Figure 2 with corresponding reference signs. Separation of hydrogen by Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The only difference is that the rest gas 133 is used as recycle-gas to the WGS 6. Process simulations have been made for recycle of 50%, 80% and 90% of rest gas to WGS. However,  
20 embodiments include using any feasible recycle ratio of the rest gas.

### Embodiment Example 9

Figure 9 shows a method for production of hydrogen from natural gas with separation of CO<sub>2</sub> according to Embodiment Example 9 which may be identical to Embodiment  
25 Example 2 except that the rest gas 134 from the cryogenic CO<sub>2</sub> separation 13 is recycled to the membrane unit 12. The syngas production, by the ATR 2, GHR 1 and ASU 5, and natural gas treatment by removing sulfur 3 and pre-reforming 4, and water-gas shift 6, may be as described in Figures 1 and 2 with units with corresponding reference signs. Further, compression of hydrogen 11 and CO<sub>2</sub> 9 may be as described in Figure 2 with corresponding reference signs. Separation of  
30 hydrogen by the Pd-membrane 12, water condensation 7 and cryogenic CO<sub>2</sub> separation may be as described in Figure 4 with corresponding reference signs. The

only difference is that the rest gas 134 is used as recycle-gas to the membrane unit 12. Process simulations have been made for recycle of 50%, 80% and 90% of rest gas to the Pd-membrane. However, embodiments include using any feasible recycle ratio of the rest gas.

#### 5    **Embodiment Example 10**

Embodiment Example 10 is identical to Embodiment Examples 5-7 except that the oxygen feed 51 is kept constant compared to Embodiment Example 2. This reduces the exit temperature from the ATR 2 from 1020 °C to, respectively, 1008 °C, 999 °C, 989 °C and 974 °C for 30%, 50%, 80% and 90% recycle.

#### 10    **Comparison of Embodiment Examples 2, 6, 8, 9 and 10**

Table 6, in Figure 15, summarizes 80% recycle of rest gas from CO<sub>2</sub> separation compared to no recycle. The recycle is to the ATR, WGS and Pd-membrane respectively. For recycle to ATR, the oxygen feed has been increased in Embodiment Example 6 to keep the exit temperature constant. The following  
15    surprising advantageous effects are found:

- Hydrogen production increases significantly for all recycle cases.
- Carbon capture rate increases significantly for all recycle cases.
- Very high capture rates are obtained when recycle is to ATR or WGS.
- Recycle to ATR without increasing oxygen flow is beneficial.
- 20    • More energy for fired heater is available when recycle is to Pd-membrane.

#### **Embodiment Example 11**

Figure 16 shows a system according to Embodiment Example 11.

Embodiment Example 11 is directed towards producing ammonia 141 and is similar to all previous Embodiment Examples in that a Pd-membrane 12 is used to separate  
25    hydrogen, the syngas is produced by a combination of GHR 1 and ATR 2, and there is a WGS reactor(s) 6.

In the present embodiment, nitrogen 52, from the ASU 5, is combined with hydrogen, from the membrane separator 12, in an ammonia synthesis unit 14. The hydrogen

supplied to the ammonia synthesis unit 14 may be either hydrogen stream 121 or the compressed hydrogen stream 111.

A preferred implementation of the present embodiment is shown in Figure 16. This is similar to Embodiment Example 8 and has corresponding reference signs. However, 5  
embodiments also include alternatively generating the hydrogen supply using any of the other Embodiment Examples described herein, and using any recycle ratios of rest gas.

Advantages of using systems according to the present embodiment for the production of ammonia include, but are not limited to, efficient natural gas reforming 10  
by using GHR/ASU, one-step WGS reaction, hydrogen separation at the same temperature as WGS, ease of separating CO<sub>2</sub> by cryogenic cooling, high hydrogen productivity and low CO<sub>2</sub> emission by recycle of rest gas, and low content of inerts in the ammonia synthesis loop.

### **Embodiment Example 12**

15 The present embodiment is directed towards providing performance gains by recycling the rest gas that remains after the hydrogen and CO<sub>2</sub> separation processes.

In the present embodiment, the hydrogen separation process may be performed before the CO<sub>2</sub> separation process, and the rest gas is therefore the gas remaining after the CO<sub>2</sub> separation process. The present embodiment also includes an 20  
alternative implementation in which the CO<sub>2</sub> separation process is performed before the hydrogen separation process, and the rest gas is therefore the gas remaining after the hydrogen separation process.

The rest gas may be fed back into one or more of any of the processes performed in the hydrogen production process. For example, the rest gas may be fed back into 25  
one or more reforming process, water-gas-shift process, hydrogen separation process and CO<sub>2</sub> separation process.

All of the rest gas may be recycled by feeding it back into one or more of the processes performed in the hydrogen production process. Alternatively, only a portion of the rest gas may be recycled. The portion of the rest gas that is recycled 30  
may be at least 50%, preferably at least 80%, and more preferably at least 90%.

In the present embodiment, any reforming process may be used. In particular, the reforming process may only comprise an autothermal reforming process.

In the present embodiment, any hydrogen separation process and CO<sub>2</sub> separation process may be used. In particular, the hydrogen separation process may be a PSA  
5 process. The CO<sub>2</sub> separation process may be a cryogenic process.

In the present embodiment, the hydrogen separation process is not restricted to being performed before the CO<sub>2</sub> separation process. Embodiments include the CO<sub>2</sub> separation process alternatively being performed before the hydrogen separation process and the rest gas being the remaining gas following the hydrogen separation  
10 process. Some, or all, of the rest gas may be recycled as described above.

The embodiments presented throughout the present document provide advantageous methods and systems for the production of hydrogen and/or ammonia. In particular, the use of a Pd-membrane to separate hydrogen immediately downstream of a WGS reactor has a surprising synergistic effect. Contrary to known  
15 techniques, the WGS reactor may be operated at substantially the same temperature as the Pd-membrane. The WGS reactor may be operated under conditions that are more preferable for the effective operation of the Pd-membrane and this can substantially improve the overall efficiencies and effectiveness of the system.

In a particularly preferred implementation according to an embodiment, the hydrogen  
20 separation process uses a hydrogen separation device as disclosed in the published patent application WO2020/012018A1, the entire contents of which are incorporated herein by reference. The hydrogen separation device disclosed in WO2020/012018A1 uses Pd-membranes to separate hydrogen from a gas mixture. The operational capabilities of the hydrogen separation device disclosed in  
25 WO2020/012018A1 result in it being particularly suitable for use in the hydrogen and/or ammonia production processes according to embodiments.

Other particularly advantageous techniques that may be used in methods and systems according to embodiments are the recycling of the rest gas directly to the Pd-membrane separator and/or water gas shift (WGS) reactor.

Embodiments include a number of modifications and variations to the above  
30 described techniques.

Embodiments may use a Pd-membrane separator 12 to separate hydrogen from shifted gas. Optionally, a sweep gas may be used on the permeate side of the membrane. The sweep gas may be steam. The steam may be at an elevated total pressure above 5 bar, preferably above 10 bar.

- 5 Embodiments include the use of a water separator, such as a condenser, in between the Pd-membrane separator 12 and the hydrogen compressor 11 to separate hydrogen from the used sweep gas.

Embodiments also include optionally using a sweep gas on the retentate side of the membrane.

- 10 In embodiments, a) sulfur may be removed from the feed gas, b) the feed gas may be saturated with water, c) hydrogen may optionally be added to the gas stream before pre-reforming the gas that has been subject to treatments a and b, d) the gas from c may be reformed by a combination of gas-heated reforming and autothermal reforming, e) the reformed gas may be subjected to water-gas-shift to give a shifted  
15 gas, f) hydrogen may be separated from the shifted gas using a Pd-membrane, g) carbon dioxide may be separated from the shifted gas that has been subject to treatment f, h) the separated hydrogen is optionally compressed and liquefied, i) the separated carbon dioxide is optionally compressed and liquefied.

- In embodiments, at least part of the rest gas from separating hydrogen and carbon  
20 dioxide may be recycled.

In embodiments, the portion of the rest gas that is recycled may be more than 50%, preferably around 80%, more preferably at least 90%. Embodiments include all of the rest being recycled.

- In embodiments, the rest gas that is recycled may be fed back into the gas-heated  
25 reforming process.

In embodiments, the rest gas that is recycled may be fed back into the autothermal reformer, the water-gas-shift reactor(s) and/or the Pd-membrane.

In embodiments, the feed gas may be natural gas.

- In embodiments, the feed gas may be a hydrocarbon rich gaseous stream from or  
30 within an oil refinery, or a petrochemical plant.

In embodiments, the gas-heated reformer may be heated by the exit gas from an autothermal reformer.

In embodiments, the exit temperature of the reformed gas from the gas-heated reformer may be in the range 400-800 °C, preferably 450-700 °C, more preferably  
5 540-600 °C.

In embodiments, the autothermal reformer may be supplied with oxygen from an air separation unit.

In embodiments, the autothermal reformer may be supplied with oxygen or oxygen enriched air from a membrane air separation unit.

10 In embodiments, the water-gas-shift reaction may be conducted in a high-temperature-shift and a low-temperature shift reactor.

In embodiments, the water-gas-shift reaction may be conducted in one reactor.

In embodiments, the water-gas shift reactor may be operated at a temperature between 200 and 300 °C, preferably between 240 and 270 °C.

15 In embodiments, the water-gas shift reactor may be operated at a temperature between 270 and 330 °C, preferably between 290 and 310 °C, most preferably at about 300 °C.

In embodiments, no additional steam may be added between the reformer and the WGS-reactor.

20 In embodiments, the water-gas shift reactor may utilize a Cu-based catalyst.

In embodiments, the CO conversion in the WGS reactor may be at least 90%, but below 98%, more preferably below 96%.

In embodiments, hydrogen may be separated before CO<sub>2</sub> is separated from the shifted gas.

25 In embodiments, the WGS and the Pd-membrane may be operated at about the same temperature.

In embodiments, water may be separated after the Pd-membrane and not before the membrane.

In embodiments, the Pd-membrane may be operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

5 In embodiments, carbon dioxide may be separated cryogenically. The carbon dioxide may be deposited in a geological reservoir.

In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by a nearby processing plant.

10 In embodiments, optionally some, or all, of the heat required for operating any of the processes may be provided by electricity from the grid and/or electricity from renewable energy source(s).

In embodiments, nitrogen may be produced by the air separation unit.

In embodiments, nitrogen and hydrogen may be used to produce ammonia. In embodiments, methanisation may be substantially avoided in the ammonia synthesis.

Embodiments include the following numbered clauses:

15 1. A method of producing hydrogen, the method comprising:

receiving a feed gas comprising hydrocarbons;

20 performing reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide, wherein

the reforming processes comprise both a gas-heated reforming process and an autothermal reforming process, and

25 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process;

performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;

30

performing a hydrogen separation process to thereby generate hydrogen and a hydrogen-depleted shifted gas; and

performing a carbon dioxide separation process on the hydrogen-depleted shifted gas to thereby generate carbon dioxide;

wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

outputting hydrogen from the permeate side of the Palladium membrane; and

outputting hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

2. The method according to clause 1, further comprising performing a sulfur removal process on the feed gas before performing the reforming processes on the feed gas.

3. The method according to clause 1 or 2, further comprising performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas; and

the method further comprising:

optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and



optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

- 5 4. The method according to any of the preceding clauses, wherein the carbon dioxide separation process generates carbon dioxide and a rest gas, and the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one of said performed processes in the method of producing hydrogen.
- 10 5. The method according to clause 4, wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.
- 15 6. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the autothermal reforming process.
7. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the water-gas-shift process.
- 20 8. The method according to clause 4 or 5, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
9. The method according to any of the preceding clauses, wherein the feed gas is natural gas.
- 25 10. The method according to any of the preceding clauses, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
- 30 11. The method according to any of the preceding clauses, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.

12. The method according to any of the preceding clauses, wherein the autothermal reforming process is supplied with oxygen from an air separation unit.
- 5 13. The method according to any preceding clause, wherein the water-gas-shift process is conducted in one water-gas-shift reactor.
14. The method according to clause 13, wherein the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably  
10 between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C.
15. The method according to any of the preceding clauses, wherein the water-gas-shift process and the hydrogen separation process are operated at about  
15 the same temperature.
16. The method according to any of the preceding clauses, wherein no additional steam is added between the reforming processes and the water-gas-shift process.
- 20 17. The method according to any of the preceding clauses, wherein the water-gas-shift process comprises using a Cu-based catalyst.
18. The method according to any of the preceding clauses, further comprising  
25 operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.
19. The method according to any of the preceding clauses, wherein water is separated from the hydrogen-depleted shifted gas output from the hydrogen  
30 separation process.
20. The method according to any of the preceding clauses, wherein water is not separated from the shifted gas before the hydrogen separation process.

21. The method according to any of the preceding clauses, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.
- 5 22. The method according to any of the preceding clauses, wherein the carbon dioxide separation process is conducted cryogenically.
23. The method according to clause 12, or any clause dependent thereon, wherein the air separation unit is also arranged to generate nitrogen, and the  
10 method comprises generating ammonia in dependence on nitrogen output from the air separation unit and hydrogen output from the hydrogen separation process.
24. A hydrogen production plant arranged to perform the method of any of clauses  
15 1 to 22.
25. An ammonia production plant arranged to perform the method of clause 23.

The flow charts and descriptions thereof herein should not be understood to prescribe a fixed order of performing the method steps described therein. Rather,  
20 the method steps may be performed in any order that is practicable. Although the present invention has been described in connection with specific exemplary embodiments, it should be understood that various changes, substitutions, and alterations apparent to those skilled in the art can be made to the disclosed embodiments without departing from the spirit and scope of the invention as set forth  
25 in the appended claims.

**Claims:**

1. A method of producing hydrogen, the method comprising:  
receiving a feed gas comprising hydrocarbons;  
5 performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;  
performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;  
10 performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and  
15 the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more of the one or more reforming processes, the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;  
20 wherein the portion of the rest gas that is recycled is at least 50%, preferably at least 80%, and more preferably at least 90%.
2. The method according to claim 1, wherein the reforming process comprises an autothermal reforming process and/or a partial oxidation reforming process  
25
3. The method according to claim 1 or 2, wherein the reforming process comprises a gas heated reforming process.

4. The method according to any preceding claim, wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and

5 heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.

5. The method according to any preceding claim, further comprising:

10 optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and

optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;

15 wherein the pre-reforming process comprises:

optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and

20 optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.

- 25 6. The method according to any preceding claim, wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

30 outputting hydrogen from the permeate side of the Palladium membrane; and

outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

7. The method according to any preceding claim, wherein the hydrogen separation process comprises a PSA process.
8. The method according to claims 2 or 4, or any claim dependent thereon, wherein the rest gas that is recycled is fed back into at least one of the one or more reforming process, and optionally the rest gas is recycled back into the autothermal reforming process.
9. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the water-gas-shift process.
10. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
11. The method according to any of the preceding claims, wherein the feed gas is natural gas.
12. The method according to any of the preceding claims, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
13. The method according to claim 3, or any claim dependent thereon, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.
14. The method according to any preceding claim, wherein the one or more reforming processes are supplied with oxygen from an air separation unit.
15. The method according to any preceding claim, wherein the water-gas-shift process is conducted in one water-gas-shift reactor;

wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C; and

5

wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.

10

16. The method according to any preceding claim, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.

15

17. The method according to any preceding claim, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

18. The method according to any preceding claim, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.

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19. The method according to any preceding claim, wherein water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.

25

20. The method according to any preceding claim, wherein water is not separated from the shifted gas before the hydrogen separation process.

30

21. The method according to claim 6, or any claim dependent thereon, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.

22. The method according to any of the preceding claims, wherein the carbon dioxide separation process is conducted cryogenically.

23. The method according to any preceding claim, the method further comprising generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.

5 24. A hydrogen production plant arranged to perform the method of any of claims 1 to 22.

25. An ammonia production plant arranged to perform the method of claim 23.

10



## AMENDED CLAIMS

received by the International Bureau on 06 July 2021 ( 06.07.2021)

**Claims:**

1. A method of producing hydrogen, the method comprising:  
  
receiving a feed gas comprising hydrocarbons;  
  
performing one or more reforming processes on the feed gas so as to generate a reformed gas comprising hydrogen and carbon monoxide;  
  
performing a water-gas-shift process on the reformed gas so as to generate a shifted gas comprising hydrogen and carbon dioxide;  
  
performing a hydrogen separation process and a carbon dioxide separation process on the shifted gas to thereby generate separate streams of hydrogen, carbon dioxide and a rest gas; and  
  
the method further comprises recycling at least part of the rest gas by feeding at least part of the rest gas back into one or more the water-gas-shift process, the hydrogen separation process and the carbon dioxide separation process;  
  
wherein the portion of the rest gas that is recycled is at least 80%, and more preferably at least 90%.
2. The method according to claim 1, wherein the reforming process comprises an autothermal reforming process and/or a partial oxidation reforming process

3. The method according to claim 1 or 2, wherein the reforming process comprises a gas heated reforming process.
4. The method according to any preceding claim, wherein the reforming process comprises both a gas-heated reforming process and an autothermal reforming process; and  
  
heat generated by the autothermal reforming process is supplied to the gas-heated reforming process.
5. The method according to any preceding claim, further comprising:  
  
optionally performing a sulfur removal process on the feed gas before performing the reforming process on the feed gas; and  
  
optionally performing a pre-reforming process on the feed gas before performing the reforming processes on the feed gas;  
  
wherein the pre-reforming process comprises:  
  
optionally saturating the feed gas with at least water before performing the pre-reforming processes on the feed gas; and  
  
optionally adding hydrogen to the feed gas before performing the pre-reforming processes on the feed gas.
6. The method according to any preceding claim, wherein the hydrogen separation process comprises:

inputting the shifted gas to a hydrogen separator that comprises a Palladium membrane, wherein the hydrogen separator comprises a permeate side of the Palladium membrane and a retentate side of the Palladium membrane, and the shifted gas is input to the retentate side of the Palladium membrane;

outputting hydrogen from the permeate side of the Palladium membrane;  
and

outputting a hydrogen-depleted shifted gas from the retentate side of the Palladium membrane.

7. The method according to any preceding claim, wherein the hydrogen separation process comprises a PSA process.
8. The method according to claims 2 or 4, or any claim dependent thereon, wherein the rest gas that is recycled is fed back into at least one of the one or more reforming process, and optionally the rest gas is recycled back into the autothermal reforming process.
9. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the water-gas-shift process.
10. The method according to any preceding claim, wherein the rest gas that is recycled is fed back into the hydrogen separation process.
11. The method according to any of the preceding claims, wherein the feed gas is natural gas.

12. The method according to any of the preceding claims, wherein the feed gas is a hydrocarbon-rich gaseous stream from, or within, an oil refinery or a petrochemical plant.
13. The method according to claim 3, or any claim dependent thereon, wherein the temperature of the gas exiting the gas-heated reforming process is in the range 400-800 °C, preferably 450-700 °C, more preferably 540-600 °C.
14. The method according to any preceding claim, wherein the one or more reforming processes are supplied with oxygen from an air separation unit.
15. The method according to any preceding claim, wherein the water-gas-shift process is conducted in one water-gas-shift reactor;  
  
wherein, optionally, the water-gas shift reactor is operated at a temperature between about 200 and about 330 °C, preferably between about 240 and about 310 °C, such as between about 240 and about 270 °C or between about 290 and about 310 °C, and/or at about 300 °C; and  
  
wherein, optionally, the water-gas-shift process comprises using a Cu-based catalyst.
16. The method according to any preceding claim, wherein the water-gas-shift process and the hydrogen separation process are operated at about the same temperature.
17. The method according to any preceding claim, wherein no additional steam is added between the reforming processes and the water-gas-shift process.

18. The method according to any preceding claim, further comprising operating the water-gas shift process so that the CO conversion in the water-gas-shift process is at least 90%, and below 98%, more preferably below 96%.
19. The method according to any preceding claim, wherein water is separated from hydrogen-depleted shifted gas output from the hydrogen separation process.
20. The method according to any preceding claim, wherein water is not separated from the shifted gas before the hydrogen separation process.
21. The method according to claim 6, or any claim dependent thereon, wherein the Palladium membrane is operated at a temperature between 200 and 400 °C, preferably between 250 and 350 °C, more preferably between 270 and 330 °C.
22. The method according to any of the preceding claims, wherein the carbon dioxide separation process is conducted cryogenically.
23. The method according to any preceding claim, the method further comprising generating ammonia in dependence on hydrogen output from the hydrogen separation process and nitrogen output from an air separation unit.
24. A hydrogen production plant arranged to perform the method of any of claims 1 to 22.
25. An ammonia production plant arranged to perform the method of claim 23.

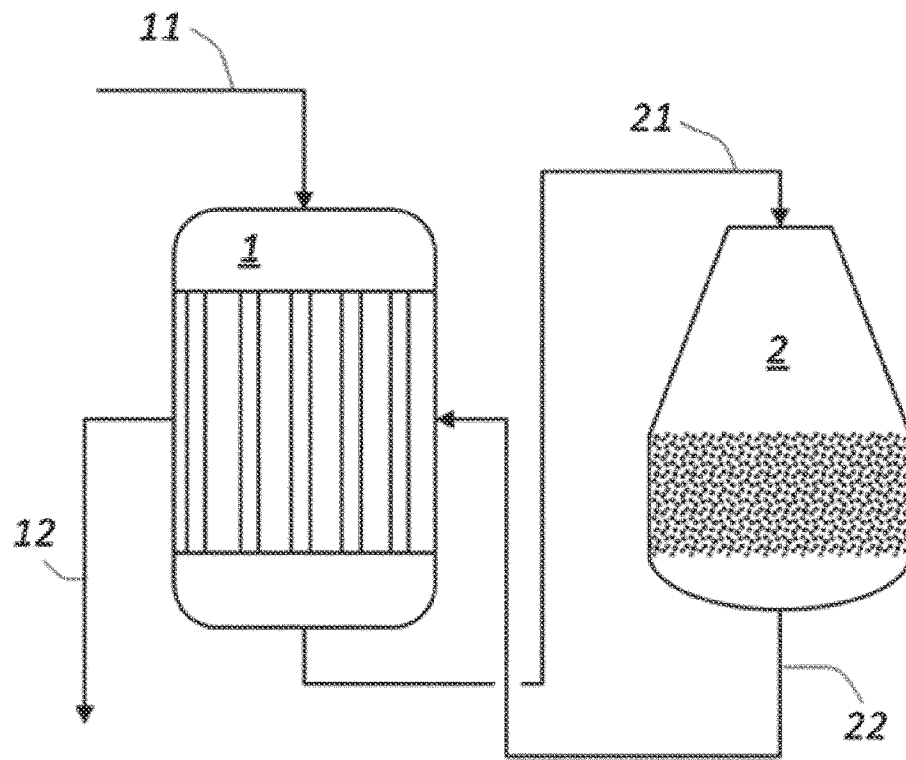


FIGURE 1

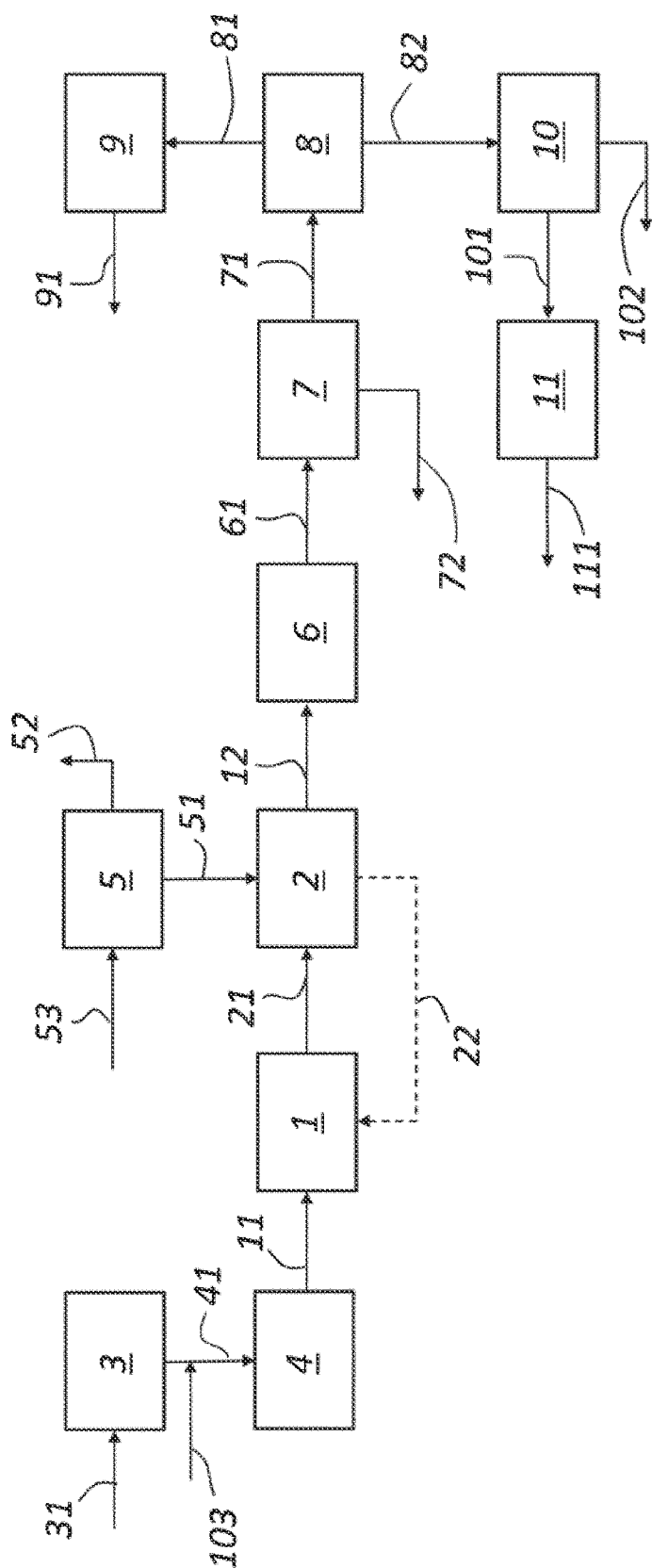


FIGURE 2

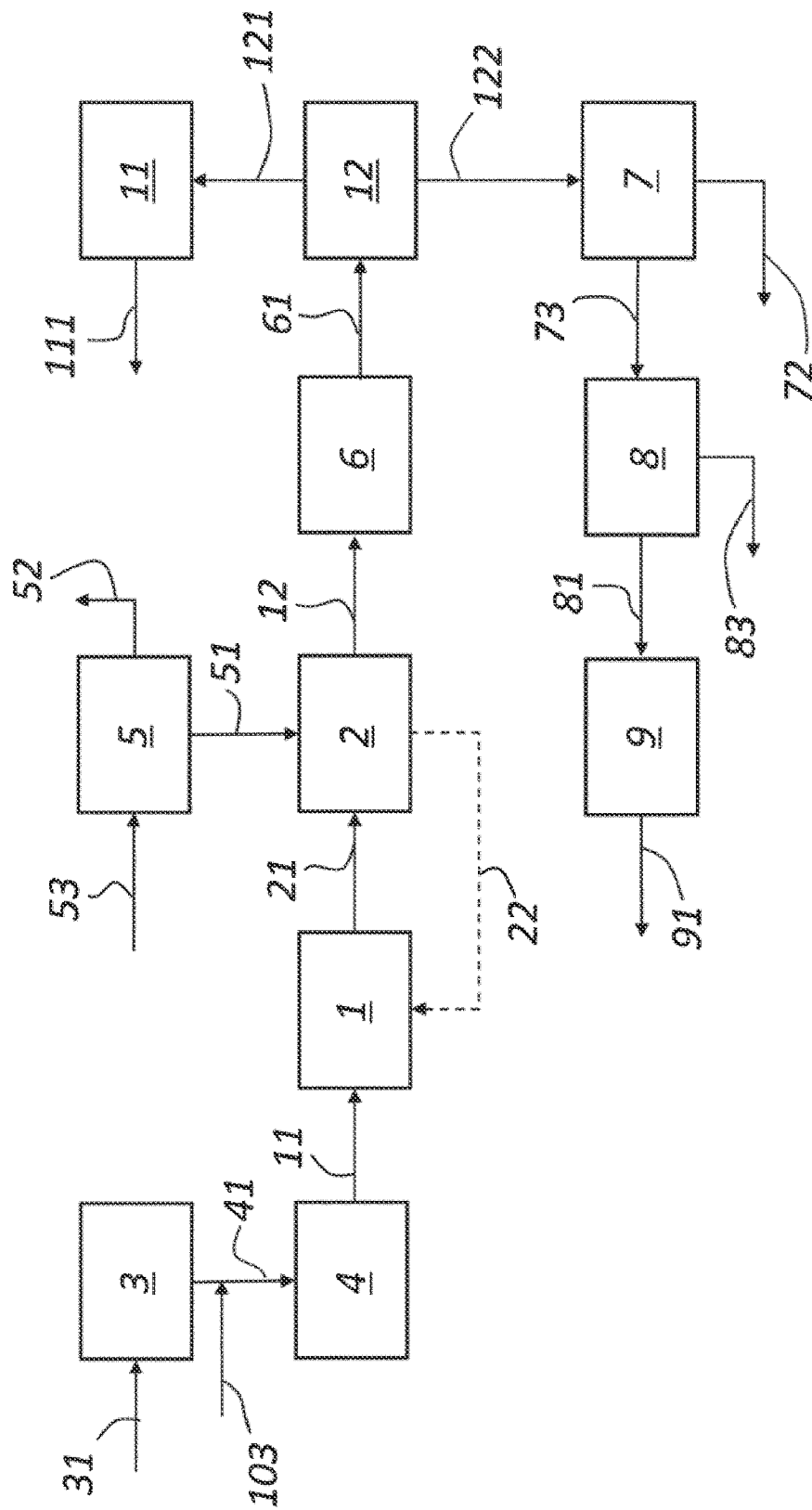


FIGURE 3



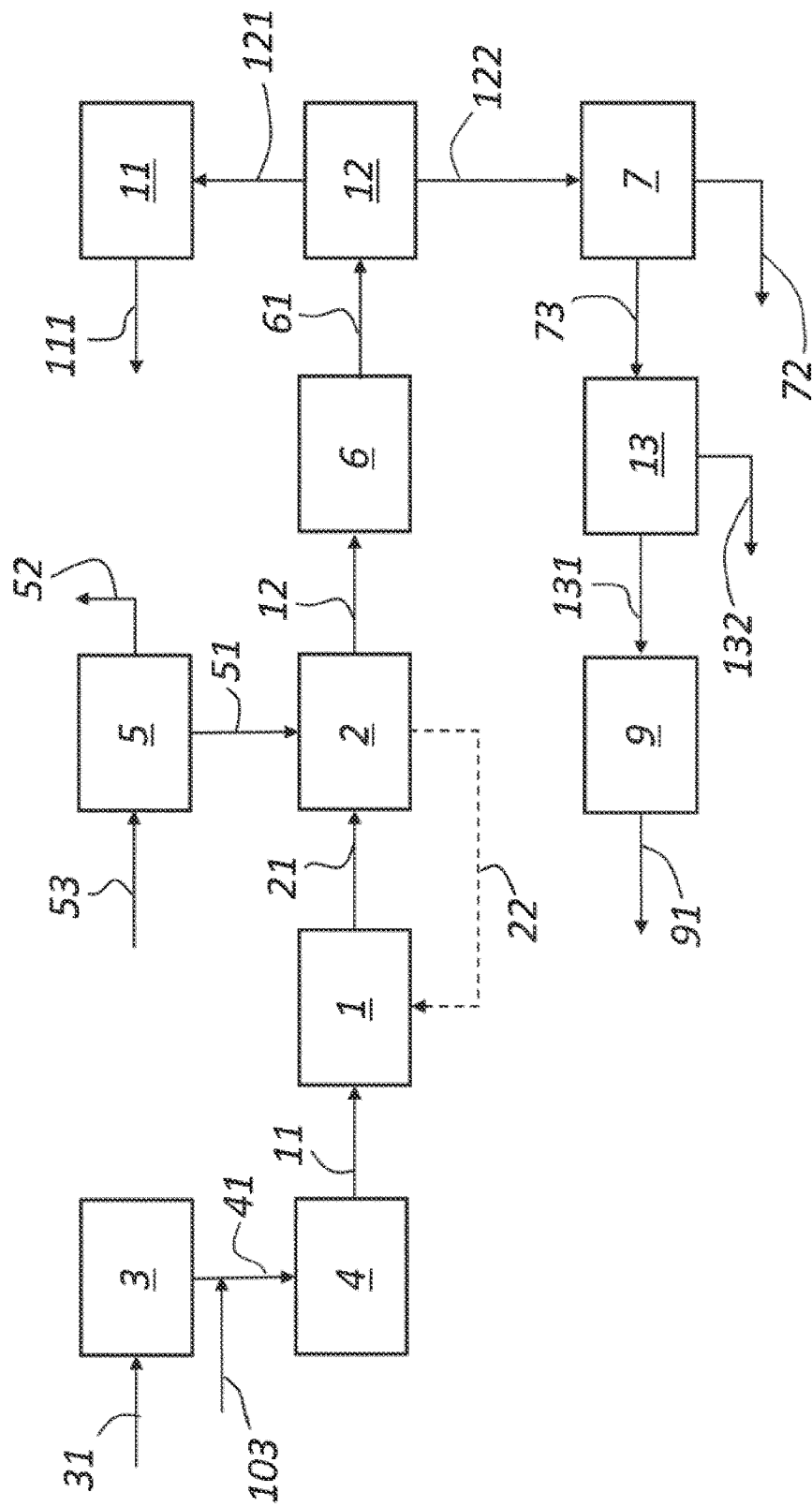


FIGURE 4

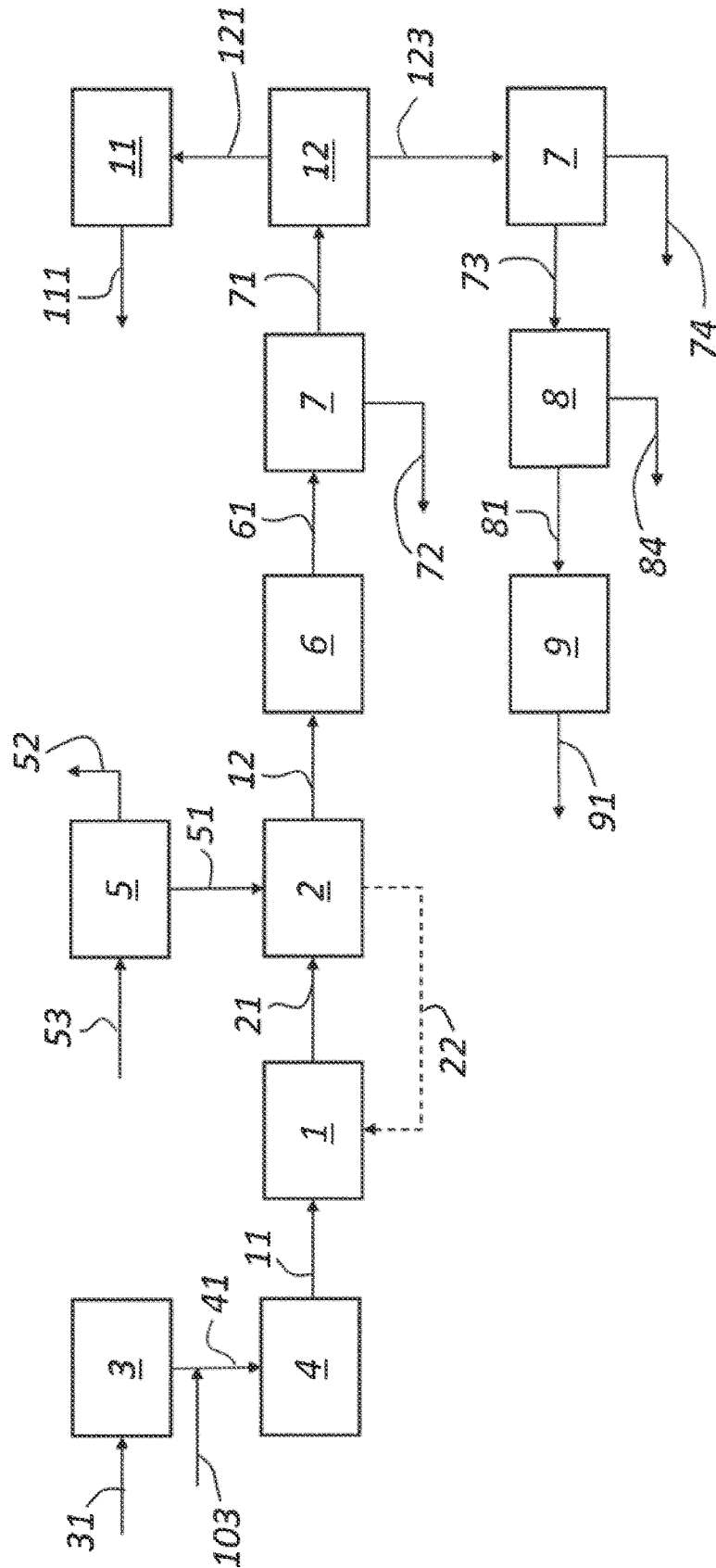


FIGURE 5

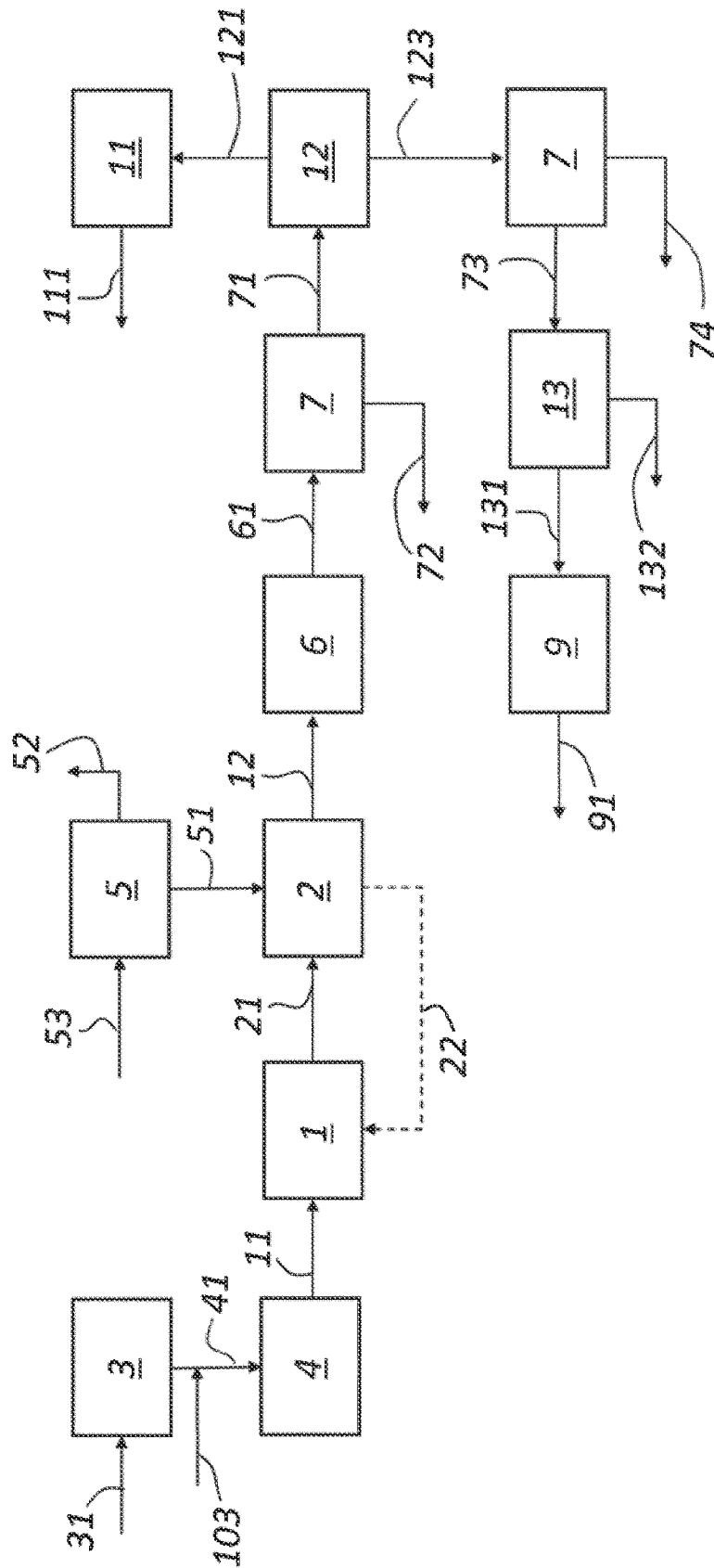


FIGURE 6

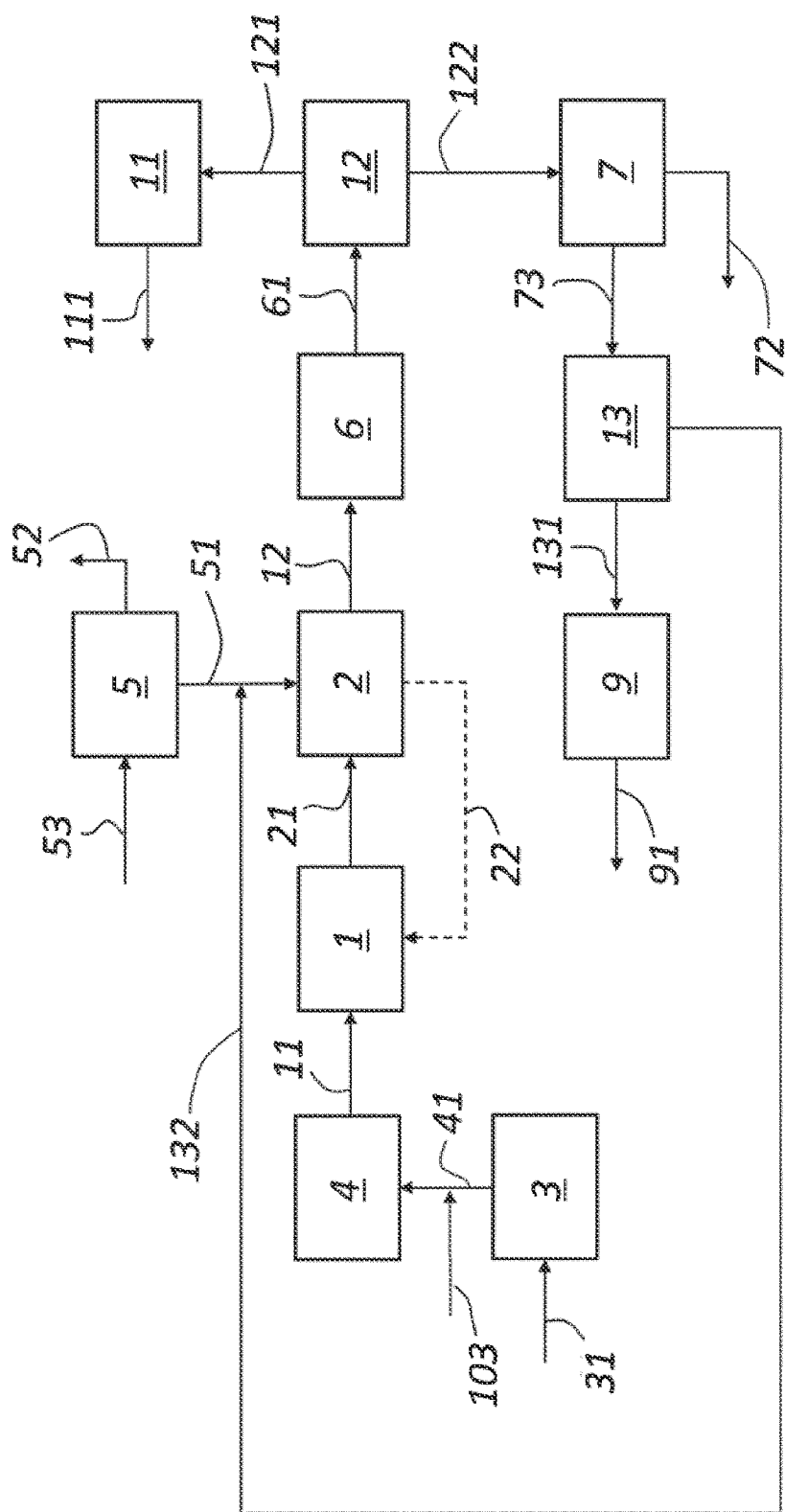


FIGURE 7

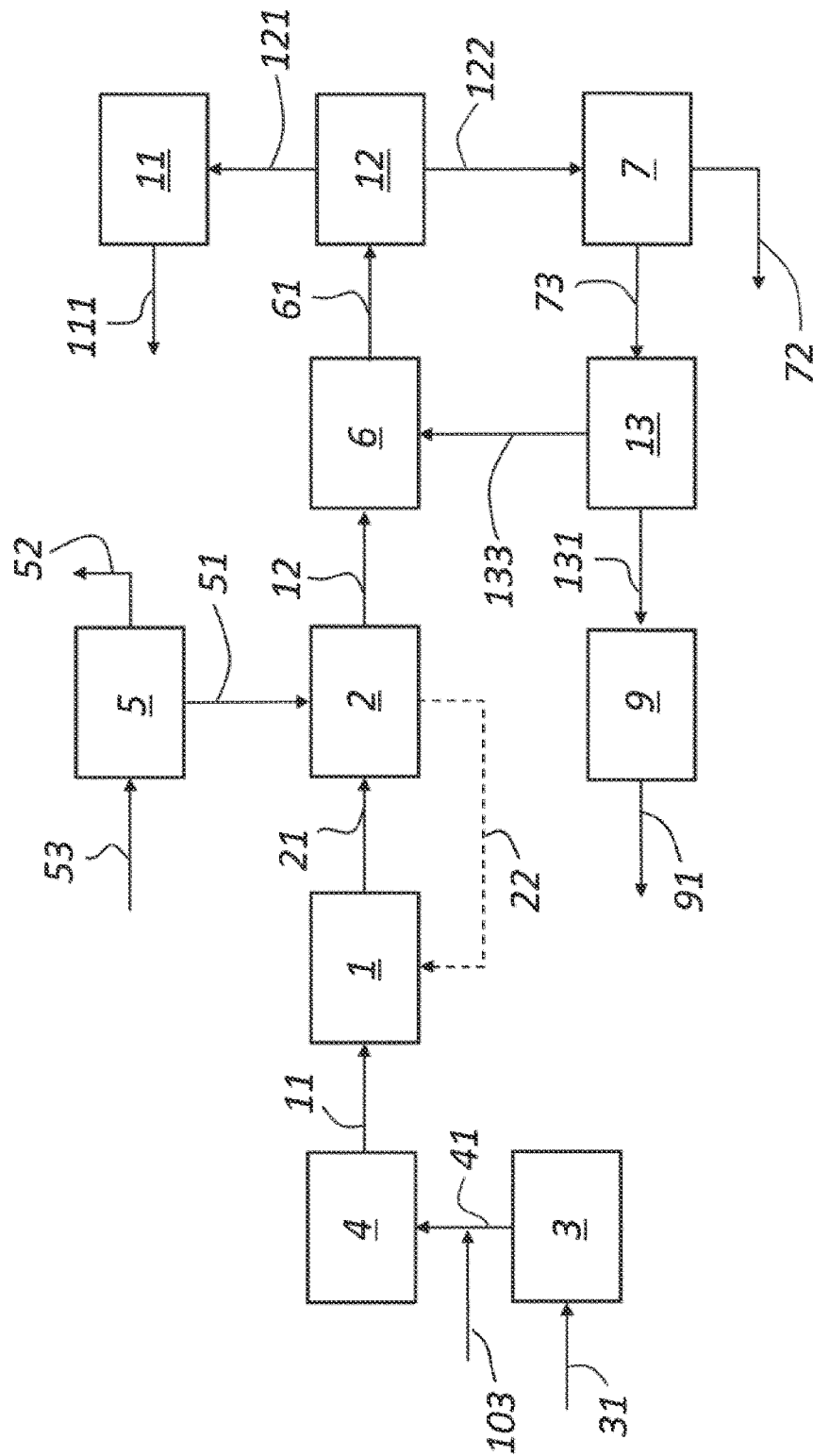
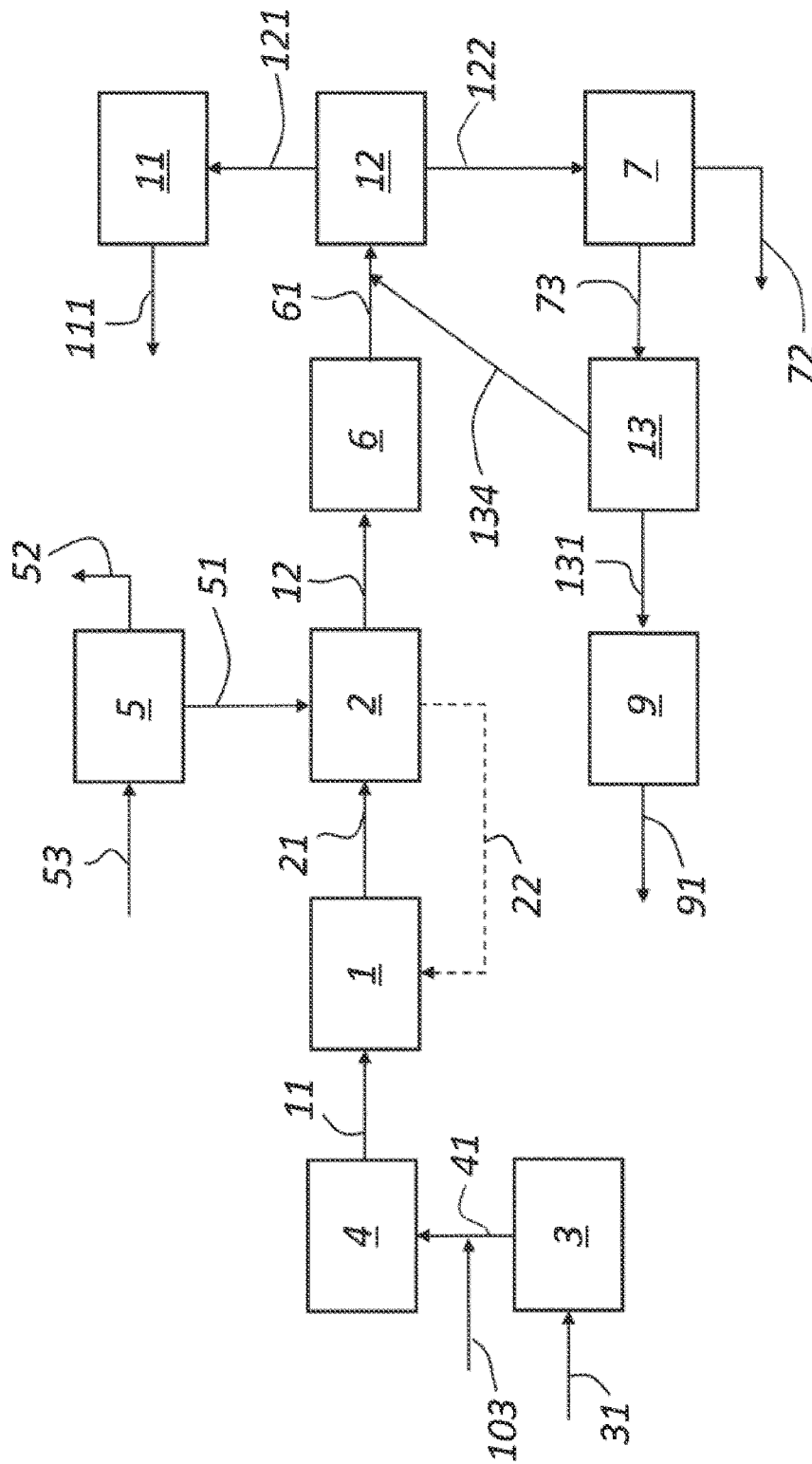


FIGURE 8



5  
E  
R  
G  
E

Table 1. Summary of process schemes.

|                                          | Comparative<br>Example | Embodiment<br>Example 1 | Embodiment<br>Example 2 | Embodiment<br>Example 3 | Embodiment<br>Example 4 | Embodiment<br>Examples 5-<br>7 |
|------------------------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------|
| WGS temperature<br>(°C)                  | 256                    | 300                     | 300                     | 256                     | 256                     | 300                            |
| Pd membrane                              |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Water condensation<br>directly after WGS | ✓                      |                         |                         | ✓                       | ✓                       |                                |
| Water condensation<br>after membrane     |                        | ✓                       | ✓                       | ✓                       | ✓                       | ✓                              |
| Amine separation                         | ✓                      | ✓                       |                         | ✓                       |                         |                                |
| Cryogenic<br>separation                  |                        |                         | ✓                       |                         | ✓                       | ✓                              |
| PSA                                      | ✓                      |                         |                         |                         |                         |                                |
| Recycle of rest-gas                      |                        |                         |                         |                         |                         | ✓                              |

FIGURE 10

Table 2.

| Type                                   | Comparative Example | Embodiment Example 1 | Embodiment Example 2 | Embodiment Example 3  | Embodiment Example 4  |
|----------------------------------------|---------------------|----------------------|----------------------|-----------------------|-----------------------|
|                                        |                     | Membrane after WGS   | Membrane after WGS   | Membrane after heater | Membrane after heater |
|                                        | Base case           | Pd + Amine           | Pd + Cryo            | Pd + Amine            | Pd + Cryo             |
| H <sub>2</sub> production (kg/h)       | 1412                | 1516                 | 1516                 | 1524                  | 1524                  |
| H <sub>2</sub> production (kmol/h)     | 701                 | 752                  | 752                  | 756                   | 756                   |
| H <sub>2</sub> recovery factor (%)     | 86                  | 93                   | 93                   | 93                    | 93                    |
| Carbon capture (%) <sup>*</sup>        | 97.5                | 96                   | 90                   | 96                    | 90                    |
| CO <sub>2</sub> before capture (mol%)  | 25                  | 79                   | 79                   | 80                    | 80                    |
| Purity of CO <sub>2</sub> captured (%) | 100                 | 100                  | 99.9                 | 100                   | 99.9                  |
| CO conversion in WGS                   | 97.4                | 95.0                 | 95.0                 | 97.4                  | 97.4                  |

<sup>\*</sup> Defined as carbon captured relative to carbon in feed

FIGURE 11



Table 3. Advantages of the different examples.

| Type                                    | Comparative Example | Embodiment Example 1 | Embodiment Example 2 | Embodiment Example 3  | Embodiment Example 4 |
|-----------------------------------------|---------------------|----------------------|----------------------|-----------------------|----------------------|
|                                         |                     | Membrane after WGS   |                      | Membrane after heater |                      |
|                                         | Base case           | Pd + Amine           | Pd + Cryo            | Pd + Amine            | Pd + Cryo            |
| Cost of H <sub>2</sub> separation       |                     | +++                  | +++                  | +++                   | +++                  |
| Footprint of H <sub>2</sub> separation  |                     | ++                   | ++                   | ++                    | ++                   |
| Efficiency of H <sub>2</sub> separation |                     | +++                  | +++                  | +++                   | +++                  |
| Cost of CO <sub>2</sub> separation      |                     | +                    | ++                   | +                     | ++                   |
| Footprint of CO <sub>2</sub> separation |                     | +                    | ++                   | +                     | ++                   |
| Efficiency of CO <sub>2</sub> capture   | ++                  | +                    |                      | +                     |                      |
| Water condensation                      | ++                  | ++                   | ++                   |                       |                      |
| Heat exchange                           | ++                  | +                    | +                    |                       |                      |
| Total                                   | 6+                  | 14+                  | 15+                  | 11+                   | 12+                  |

FIGURE 12

Table 4. Effect of recycling rest-gas to ATR.

|                                     | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Recycle option                      | No recycle              | 50%                     | 80%                     | 90%                     |
| O <sub>2</sub> to ATR (kg/h)        | 4179                    | 4316                    | 4426                    | 4482                    |
| H <sub>2</sub> production (kmol/h)  | 752                     | 777                     | 794                     | 799*                    |
| Carbon capture (%)                  | 89.7                    | 94.4                    | 97.7                    | 98.8                    |
| Heat available in Fired heater (MW) | 4.6                     | 2.5                     | 1.0                     | 0.5                     |

\* Represents 99% hydrogen recovery compared to Table 2.

FIGURE 13

Table 5. Advantages of Embodiment Examples 5-7.

|                                         | Embodiment<br>Example 2 | Embodiment<br>Example 5 | Embodiment<br>Example 6 | Embodiment<br>Example 7 |
|-----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|                                         | No recycle              | 50 %                    | 80 %                    | 90 %                    |
| Cost of H <sub>2</sub> separation       | +++                     | +++                     | +++                     | +++                     |
| Footprint of H <sub>2</sub> separation  | ++                      | ++                      | ++                      | ++                      |
| Efficiency of H <sub>2</sub> separation | +++                     | +++                     | +++                     | +++                     |
| Cost of CO <sub>2</sub> separation      | ++                      | ++                      | ++                      | ++                      |
| Footprint of CO <sub>2</sub> separation | ++                      | ++                      | ++                      | ++                      |
| Efficiency of CO <sub>2</sub> capture   |                         | +                       | ++                      | +++                     |
| Water condensation                      | ++                      | ++                      | ++                      | ++                      |
| Heat exchange                           | +                       | +                       | +                       | +                       |
| Energy efficiency                       | ++                      | +                       |                         |                         |
| Total                                   | 17+                     | 17+                     | 18+                     | 19+                     |

FIGURE 14

Table 6. Effect of recycling 80% rest-gas compared to no recycle.

|                                        | Embodiment<br>Example 2 | Embodiment<br>Example 6 | Embodiment<br>Example 8 | Embodiment<br>Example 9 | Embodiment<br>Example 10 |
|----------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| Recycle option                         | No recycle              | To ATR                  | To WGS                  | To<br>membrane          | To ATR                   |
| Recycle ratio                          | 0%                      | 80%                     | 80%                     | 80%                     | 80%                      |
| O <sub>2</sub> to ATR (kg/h)           | 4179                    | 4426                    | 4179                    | 4179                    | 4179                     |
| ATR exit (°C)                          | 1020                    | 1020                    | 1020                    | 1020                    | 989                      |
| H <sub>2</sub> production (kmol/h)     | 752                     | 798                     | 803                     | 797                     | 807                      |
| Carbon capture (%)                     | 89.7                    | 97.7                    | 97,3                    | 95,1                    | 97,5                     |
| Heat available in Fired<br>heater (MW) | 4.6                     | 1.0                     | 1,5                     | 1,9                     | 1.2                      |

FIGURE 15

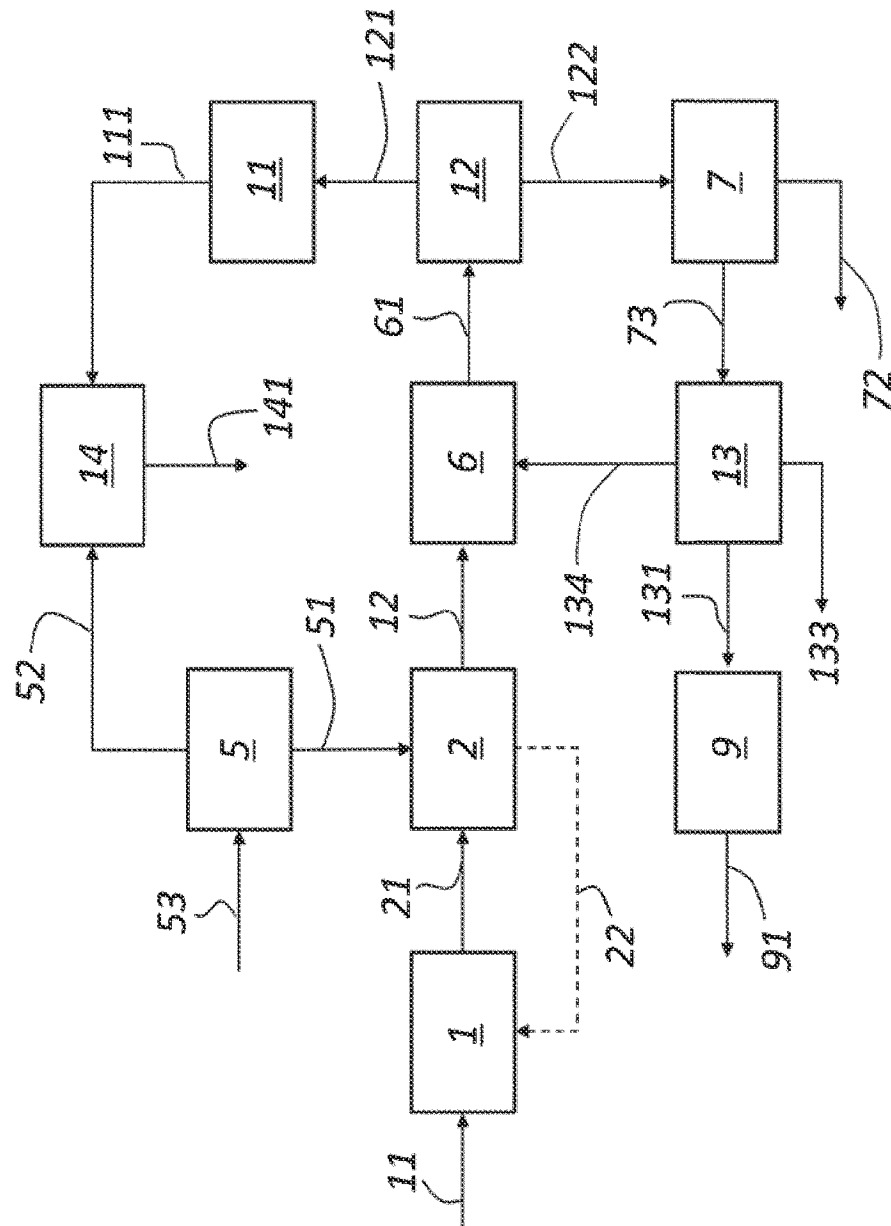


FIGURE 16

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2021/054441

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B3/48 C01B3/50  
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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                      | Relevant to claim No.             |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|
| X         | WO 2019/162236 A1 (REINERTSEN NEW ENERGY AS [NO]) 29 August 2019 (2019-08-29)<br><br>abstract<br>claims 1,2,4,7,8,10,18,21-23,27,28<br>figure 2<br><br>-----                                                            | 1-8,<br>11-14,<br>19,21,<br>22,24 |
| X         | US 2010/310949 A1 (LICHT WILLIAM ROBERT [US] ET AL) 9 December 2010 (2010-12-09)<br><br>abstract<br>figure 2<br>claims 1,2<br>paragraphs [0023], [0036], [0047],<br>[0049], [0050], [0052], [0053]<br><br>-----<br>-/-- | 1,2,5,7,<br>8,11,<br>15-19,24     |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents :

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"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

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

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Date of the actual completion of the international search

12 May 2021

Date of mailing of the international search report

25/05/2021

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Authorized officer

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2021/054441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                    | Relevant to claim No.                                |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|
| X         | <p>US 2014/170052 A1 (IAQUANIELLO GAETANO [IT] ET AL) 19 June 2014 (2014-06-19)</p> <p>abstract<br/>claims 1,3,6,8,9,11<br/>figure 2<br/>paragraphs [0023], [0036], [0039] -<br/>[0044], [0061], [0062]<br/>-----</p> | <p>1,2,5,7,<br/>8,11,12,<br/>14-18,<br/>20,23-25</p> |
| X         | <p>US 8 715 617 B2 (GENKIN EUGENE S [US];<br/>HERSHMAN PATRICIA KENTOSH [US] ET AL.)<br/>6 May 2014 (2014-05-06)<br/>claims 1-3<br/>figure 2<br/>column 6 - column 10<br/>-----</p>                                   | <p>1,2,5,<br/>7-12,<br/>14-19,24</p>                 |
| X         | <p>US 6 090 312 A (ZIAKA ZOE D [US] ET AL)<br/>18 July 2000 (2000-07-18)</p> <p>figure 1<br/>claims 1,4<br/>column 1, lines 7-23<br/>column 2, line 66 - column 3, line 32<br/>-----</p>                              | <p>1,8,11,<br/>12,<br/>17-19,24</p>                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/054441

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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|                                           |                     | EP 2723676 A1              | 30-04-2014          |
|                                           |                     | LT 2723676 T               | 12-03-2019          |
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|                                           |                     | WO 2012177137 A1           | 27-12-2012          |
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