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[Continued on next page]

(54) Title: A PROCESS AND A REACTOR DESIGN FOR AMMONIA PRODUCTION USING AMMONIA SELECTIVE MEMBRANES

(57) Abstract: In a process for ammonia production by separating residual NH_3 from N_2, H_2, CH_4 and Ar in the recycle gas of an ammonia plant in a membrane system, the separation is carried out in the recycle line of an ammonia converter with the membrane system located at a point after cooling and condensing of the ammonia. In this way impurities are removed from the gas, and a feed gas with low NH_3 content to be fed to the converter is obtained. The membrane system consists of one or more low temperature, high pressure ammonia selective membranes with an ammonia/H_2 selectivity of at least 4, and NH_3 on the permeate side is removed by pumping or with the aid of a sweep gas.

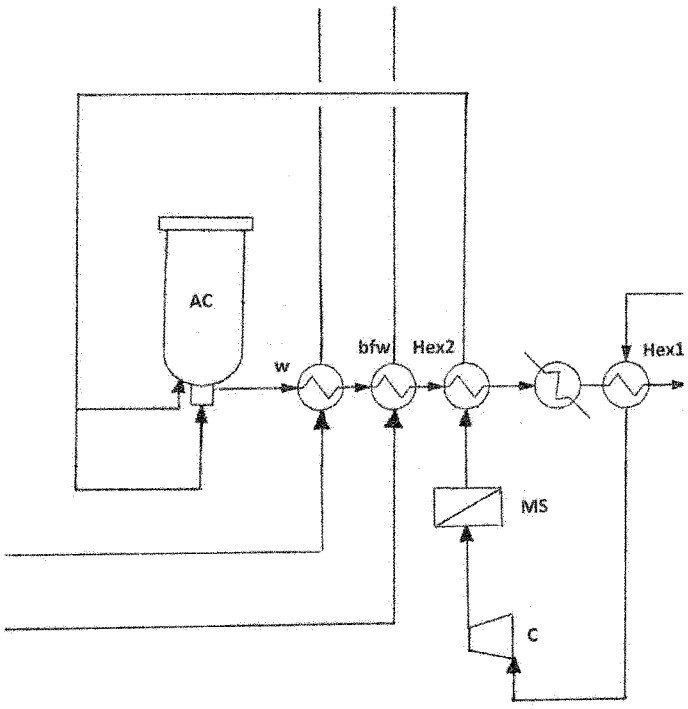

Fig. 1

WO 2016/198367 A1

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

Title: A process and a reactor design for ammonia production using ammonia selective membranes

The present invention relates to a process and a reactor design for ammonia production using ammonia selective membranes. More specifically, a membrane system is used which consists of one or more low temperature, high pressure ammonia selective membranes with an ammonia/H_2 selectivity of at least 4. Such ammonia selective membranes may be membranes consisting of polymer-based organic materials, but they may alternatively be membranes based on inorganic materials.

The catalytic synthesis of ammonia from hydrogen and nitrogen according to the equation

$$N_2 + 3H_2 <-> 2NH_3 \ (\Delta H = -92.4 \text{ kJ/mol})$$

was developed around 1908 and improved to industrial scale a few years later. Since then, this method (the Haber-Bosch method) has been the predominant industrial scale method for ammonia production. The synthesis is carried out in a circulatory system commonly known as an ammonia synthesis loop. Only a fraction of the synthesis gas is converted per pass, as limited by the equilibrium concentration of NH_3 at the exit conditions of the converter.

In general, the make-up gas fed to the loop will contain about 99% of nitrogen and hydrogen in a molar ratio H_2/N_2 of around 3.0 with about 1% methane and argon besides minor amounts of other molecules, some of which may be catalyst poisons.

The catalytic activity of an ammonia catalyst may be reduced in the presence of certain chemical compounds (poisons). These may be gaseous, occurring as minor components of the synthesis gas, or they may be solids introduced as impurities to the catalyst during the manufacturing process.

In the case of gaseous catalyst poisons, a distinction can be made between permanent poisons (causing an irreversible loss of catalytic activity) and temporary poisons (lowering the activity only while present in the synthesis gas). Permanent poisons such as sulfur accumulate upon the catalyst surface and may be detected by chemical and spectroscopic analysis, while temporary poisons such as oxygen, carbon and water do not interact as strongly with the catalyst. The concept of catalyst poisoning is dealt with in chapter 8 of "Catalytic Ammonia Synthesis", edited by J.R. Jennings, Plenum Publishing Corporation (1991).

The deactivation of the ammonia catalyst is dependent on the operating conditions (pressure and temperature), but more significantly on the small amounts of gaseous compounds contained in the feed gas. It is therefore imperative that such compounds are removed from the feed gas and that a feed gas with low NH_3 content to be fed to the converter is obtained.

The average lifetime of an ammonia synthesis catalyst has increased markedly since the early days of ammonia manufacture due to a number of process improvements. One of these is the incorporation of a secondary ammonia condensation

system, in which the make-up gas together with the recycle gas is washed in liquid ammonia before entering the ammonia synthesis converter.

There are a number of industrial processes in which it is necessary to separate NH_3 from mixtures of other gases. Perhaps the largest scale separation is the removal of NH_3 from the gas mixture that is present in the recycle loop of an ammonia synthesis plant. This separation is currently accomplished by refrigeration, with ammonia being condensed and removed in a liquid state. Thus, in the conventional ammonia synthesis procedure, ammonia is separated from the synthesis gas by cooling, typically to a temperature of around -28°C which condenses the ammonia, using an ammonia cooling system. The condensed ammonia also serves as a final purification of the make-up gas since it removes trace components water and carbon dioxide.

It has previously been proposed to use membranes for separation of ammonia from the synthesis gas; however, a system like that will not protect the synthesis gas against trace amounts of poison, such as water and carbon dioxide coming from the methanation reactor.

In the process according to the invention, ammonia selective membranes are used after the ammonia condenser on the feed gas to the converter. The ammonia content in the gas will typically be around 4%, and the membrane system will remove the ammonia to below 2%. Thus the conversion per pass can be increased significantly.

EP 1 083 150 A1 discloses a process for producing ammonia in a recycle circuit stream which comprises at least hydrogen and nitrogen and also at least a portion of the ammonia formed as a product. The ammonia is abstracted from the recycle circuit stream by means of a ceramic membrane unit. The process starts from a hydrogen and nitrogen containing feed, wherein (a) the feed is fed into a recycle circuit stream, the recycle circuit comprising at least one reactor in which ammonia is formed from hydrogen and nitrogen, and (b) the ammonia is abstracted from the recycle circuit stream leaving the reactor, after which the recycle circuit stream is fed back to the reactor. Furthermore (c) the recycle circuit incorporates a membrane unit, which is permeable at least to ammonia. The recycle circuit stream is passed through the membrane unit on one side of the membrane and the feed is passed through the membrane unit on the other side of the membrane in such a way that at least ammonia from the recycle circuit stream is incorporated into the feed.

Figs. 2 and 3 of EP 1 083 150 A1 show a recycle circuit operating at pressures and temperatures similar to those of the present invention, with a pressure differential across the ceramic membrane of between 25 and 350 bar, the recycle circuit forming the ‘high pressure side’ and the feed side forming the ‘low pressure side’. The operation temperature is from -10°C to 100°C. The action of the membrane ensures that ammonia in the recycle gas diffuses through the membrane, thereby lowering the concentration of ammonia in the recycle circuit stream to the inlet of the reactor. This results in an increased ammonia production.

According to EP 1 083 150 A1, the membrane is placed between the recycle gas and the make-up gas, either before (Fig. 2) or after (Fig. 3) the first compressor. In the first case, the gas is cooled after the first compressor step and the ammonia is condensed out together with i.a. water. In the second case, the make-up gas, now containing ammonia, is sent to the second compressor step, and from there it moves on to be mixed with the exit gas from the converter to the separator. Especially this second case cannot be favourable because the make-up gas stream is about 5 times smaller than the recycle gas stream, and the partial pressure difference will soon be very small. This means that only a limited amount of the ammonia will be captured via the membrane.

The process steps and the advantages obtained according to EP 1 083 150 A1 are rather similar to those of the present invention, but the EP publication only discloses use of a ceramic membrane, not a polymeric membrane or a combined polymeric/ceramic membrane. The membranes described in EP 1 083 150 A1 are not described as being low temperature or high temperature membranes, nor is the ammonia/H_2 selectivity of these membranes described.

US 4.758.250 A discloses a process for ammonia separation using polymeric ion exchange membranes and sorbents from an ammonia synthesis plant recycle loop gas. It is not clearly stated where the membrane is located in the recycle loop.

In US 5.455.016 a polymeric membrane is disclosed, which is positioned before the compressor for the feed to the converter. There is no disclosure regarding the pressure in

the recycle streams. However it is stated that recycling with a lower ammonia concentration has the effect that the productivity of the reactor in terms of ammonia conversion per pass is increased.

EP 0 293 736 A2 describes the separation of ammonia from mixtures containing ammonia and other gases, such as nitrogen and hydrogen, using semipermeable ion exchange polymeric membranes and sorbents. The active materials in said semipermeable membranes may also be used as selective NH_3 sorbents for the recovery of ammonia from such mixtures.

Finally, US 6.065.306 discloses a method of producing a purified, pressurized ammonia stream from a feed stream comprising ammonia, moisture and other impurities. The method is more focused on treatment of the ammonia exiting the converter than on the removal of residual ammonia from the recycle gas.

The previously suggested applications of polymer-based ammonia selective membranes have mainly looked at the ammonia membrane as an alternative to the removal of ammonia based on condensation, which is used today. However, this is a dubious way of using the membrane. First of all, the benefit of final purification of the make-up gas by washing it in liquid ammonia is lost and, secondly, the membrane system will be very large. The system proposed with the present invention includes the best of the previous practice along with a new membrane system.

The present invention is based on the idea that the membrane system is to be placed at a point after cooling and

condensing of the ammonia, thereby both removing impurities from the gas and obtaining a feed gas with low NH_3 content to be fed to the converter.

In connection with the present invention, possible membrane types to separate the residual NH_3 from N_2, H_2, CH_4 and Ar in the recycle gas of an ammonia plant have been investigated. The purpose was to be able to increase the ammonia production in the synthesis loop. Basically there are two types of membranes: i) inorganic materials, such as $MgCl_2$ and zeolites, and ii) organic polymers. The inorganic materials are recommended for high temperature applications, whereas the polymers are suitable for low temperature applications. In the present invention, the target temperature is 0 to 35°C.

Previous investigations within the field of gas phase NH_3 removal from other gases have been very sparse. Some of the attempts have been directed to incorporating the inorganic membranes right at the exit of the ammonia synthesis reactor to overcome the thermodynamic equilibrium limitations. However, these attempts could not identify a suitable membrane with the right permeance selectivity to NH_3 at temperatures above 300°C with the mixed gas feeds. As one of the best cases with inorganic membranes, an ammonia/H_2 permeance ratio of 30 was obtained at 50°C with a silica membrane that had 0.35 nm pores.

Organic polymer based membranes have shown higher permeance selectivities. Thus, an ammonia/H_2 permeance selectivity of 90 at 25°C obtained with block-copolymer membranes has been reported. One of the best cases presented is a polyvinyl-

ammonium thiocyanate membrane having an ammonia/H_2 permeance selectivity of 1500 at 25°C. The mechanism of this membrane type was investigated in J. Am. Chem. Soc. 113, 742-749 (1991). This investigation also found that Nafion® (perfluorosulfonic acid) membranes could have a selectivity of 500 at 25°C.

The idea underlying the present invention has been to find out whether any membrane technologies could be implemented in the recycle line of an ammonia converter. It has not been considered to separate the ammonia at the reactor exit, but rather to purify the recycle gas from residual ammonia, thereby being able to increase the reactor yield.

The most critical factors when designing a low temperature, high pressure membrane for ammonia separation are:

- Membrane permeance: This depends on the gas composition, the temperature, the pressure and the physical characteristics of the membrane.

- Membrane stability: For the purposes of the invention, stability against high pressure is very important. This can be achieved by depositing the membrane polymer on a porous support and then topping the membrane surface with a non-selective and very permeable polymer layer to prevent cracking or pinhole formation on the selective membrane layer.

- Membrane selectivity: Especially the ammonia/H_2 selectivity should minimum be 4.

Thus, the present invention relates to a process for ammonia production by separating residual NH_3 from N_2, H_2, CH_4 and Ar in the recycle gas of an ammonia plant in a membrane system,

wherein the separation is carried out in the recycle line of an ammonia converter with the membrane system located at a point after cooling and condensing of the ammonia, thereby both removing impurities from the gas and obtaining a feed gas with low NH_3 content to be fed to the converter,

wherein the membrane system consists of one or more low temperature, high pressure ammonia selective membranes with an ammonia/H_2 selectivity of at least 4, said ammonia selective membranes consisting of polymer-based organic materials, and

wherein NH_3 on the permeate side is removed by pumping or with the aid of a sweep gas.

More specifically, on the permeate side of the membrane, NH_3 is removed either by pumping to ensure a constant and low pressure of NH_3 or with a sweep gas consisting of either CO_2, N_2, H_2O, ethane, propane, butane, pentane or any combination of these.

The invention further relates to a reactor design for ammonia production, said design comprising at least one ammonia converter (AC), a heat exchanger (Hex2), a loop waste heat boiler (w), a loop boiler feedwater preheater (bfw), a compressor (C) and a membrane system (MS).

The reactor design according to the invention is shown in the figure, which illustrates a part of the ammonia synthesis loop. The membrane system would most suitably be located at a low temperature part of the ammonia synthesis loop before the gas arrives to the compressor (C) and the heat exchanger (Hex2). At this point the gas is cold after having passed a first heat exchanger (Hex1). However, it is preferably located after the compressor, which condenses the ammonia in the gas before the gas enters the heat exchanger (Hex2). The figure shows this latter possible location of the membrane system (MS).

Organic polymer-based membranes can be used at low temperatures, which provide somewhat higher permeance selectivities of NH_3 in comparison to the inorganic membranes. The higher permeability of NH_3 in polymers results from its solubility in salts and ionic polymers. N_2 and H_2, which are less polar, are less soluble. A potential problem when using these polymer membranes could be their stability under high pressures (180-190 bar). However, this problem can be circumvented by depositing the polymer onto a microporous support with large pores to avoid mass transfer limitations. Given the flow and sweep gas rates in a membrane cell and knowing the permeabilities of the gases in the gas mixture, it is possible to calculate the surface area and hence the thickness of the membrane needed for a certain application. An example of such calculation can be found in J. Membrane Sci. 104, 19-26 (1995).

The invention is illustrated in more detail in the following examples. However, the invention is not limited to these specific examples.

Example 1

In an ammonia plant, the feed gas to the converter is compressed in a recirculation compressor to a pressure of 18.6 MPa and a temperature of 40°C. The ammonia content is typically in the order of 4 vol% corresponding to a partial pressure of 0.75 MPa.

The feed gas is introduced into a membrane unit in which the ammonia is removed down to a partial pressure of 0.2 MPa corresponding to 1 vol% in the feed gas. The ammonia from the membrane is cooled and compressed and then sent to the product ammonia tank.

The resulting feed gas is more reactive, and thus the inlet temperature to the converter can be lowered by 10-20°C. The higher conversion per pass will also result in a smaller flow, which may be used either to be able to use smaller converters or alternatively to reduce the synthesis pressure.

Example 2

A residual recycle gas contains about 4% NH_3, 66% H_2, 22% N_2, 5.4% CH_4 and 2.6% Ar. Before arriving to the compressor (C), the gas has a temperature between 0 and 35°C under a pressure of 186 bar. After the compressor, the gas passes the membrane system (MS), and a heat exchanger (Hex) heats the gas to 232°C. Then the gas enters the ammonia converter (AC), where the exit composition from the converter is found to be 17.8% NH_3, 53.4% H_2, 17.8% N_2, 6.3% CH_4 and 2.9%

Ar. The exit gas is then cooled to condense the ammonia, and the residual gas is recycled into the converter.

Applying the same assumptions as used in J. Membrane Sci. 104, 19-26 (1995) regarding membrane area and space time needed to remove a certain amount of ammonia with a given membrane system, the following results are obtained:

Based on the flow diagram shown in the figure and assuming that the ammonia concentration is to be decreased from 4% to 1% with a membrane having an ammonia permeance of 0.01 m/s, a feed gas of 233.3 Nm^3/s at a total pressure of 186 bar and with a permeate pressure of 1 bar NH_3, a membrane area of 46000 m^2 would be the result. Assuming a Nafion® membrane of 150 m2/g, this corresponds to 306 g of Nafion® deposited on a porous carrier. Further assuming a thickness of 36 µm, the diameter of the potential membrane can be calculated to be 236 cm (93”). This is a much higher diameter in comparison to the usual piping diameter (20”) used for an ammonia plant with a production around 2200 MTPD. However, if the membrane permeance is higher, the necessary membrane diameter can be decreased.

Claims:

1. A process for ammonia production by separating residual NH_3 from N_2, H_2, CH_4 and Ar in the recycle gas of an ammonia plant in a membrane system,

wherein the separation is carried out in the recycle line of an ammonia converter with the membrane system located at a point after cooling and condensing of the ammonia, thereby both removing impurities from the gas and obtaining a feed gas with low NH_3 content to be fed to the converter,

wherein the membrane system consists of one or more low temperature, high pressure ammonia selective membranes with an ammonia/H_2 selectivity of at least 4, said ammonia selective membranes consisting of polymer-based organic materials, and

wherein NH_3 on the permeate side is removed by pumping or with the aid of a sweep gas.

2. The process according to claim 1, wherein the ammonia selective membranes in the membrane system consist of inorganic materials.

3. The process according to claim 1, wherein NH_3 is pumped away from the permeate side to ensure a constant low pressure of NH_3.

4. The process according to claim 1, wherein the sweep gas is either CO_2, N_2, H_2O, ethane, propane, butane, pentane or any combination of these.

5. A reactor design for ammonia production by the process according to any of the claims 1-4, said design comprising at least one ammonia converter, heat exchangers (Hex1 and Hex2), a loop waste heat boiler (w), a loop boiler feedwater preheater (bwf), a compressor (C) and a membrane system (MS).

6. Reactor design according to claim 5, wherein the membrane system is located at a low temperature part of the ammonia synthesis loop before the gas arrives to the compressor and the heat exchanger.

7. Reactor design according to claim 5, wherein the membrane system is located after the compressor before the gas enters the heat exchanger.

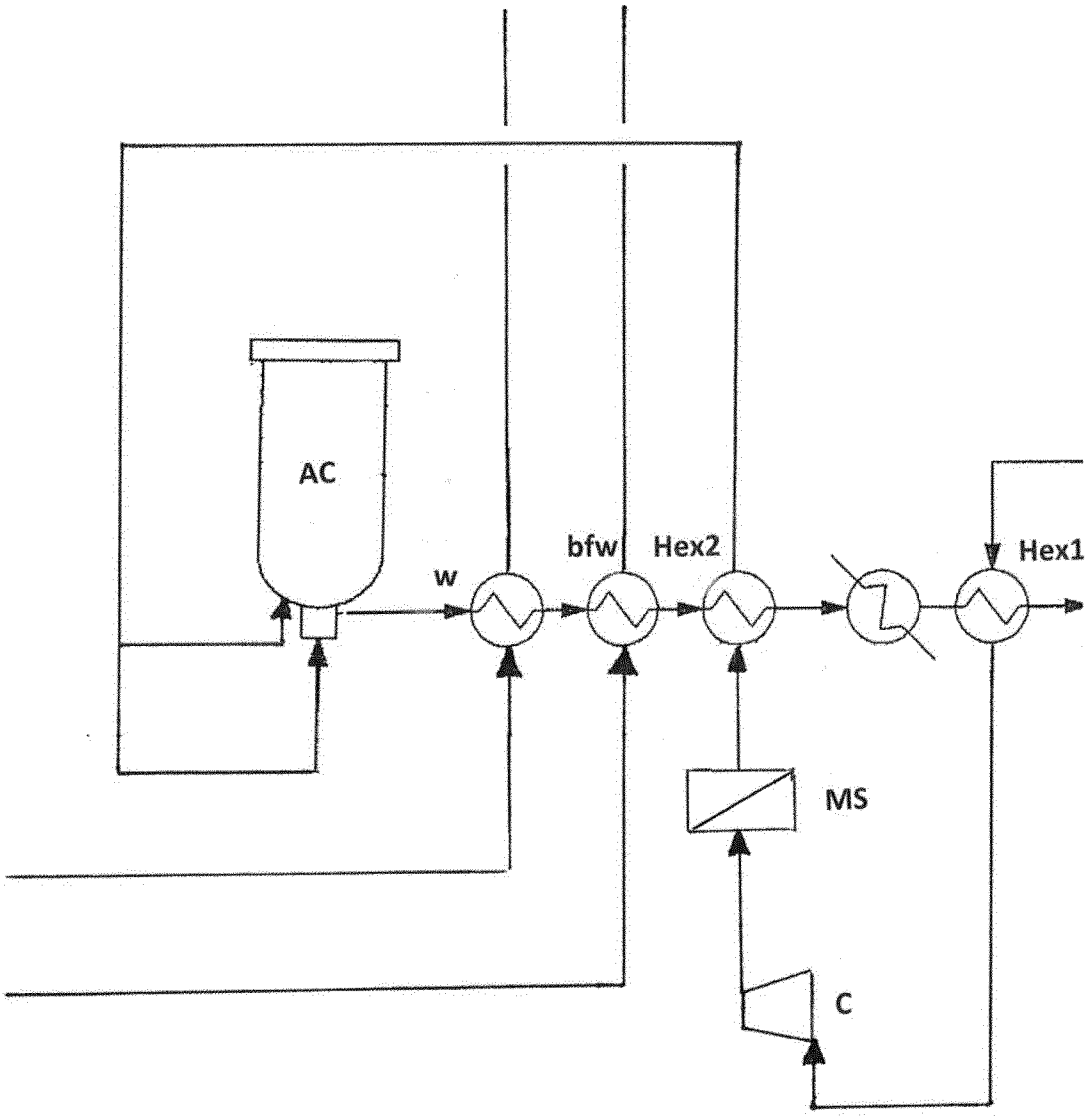

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/062827

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01C1/04 B01D53/22
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)
C01C B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 083 150 A1 (CONTINENTAL ENGINEERING B V [NL]) 14 March 2001 (2001-03-14) cited in the application paragraphs [0006] - [0010], [0016] - [0019], [0035], [0045] - [0049]; figure 2	1-7
Y	US 4 758 250 A (LACIAK DANIEL V [US] ET AL) 19 July 1988 (1988-07-19) claim 8; tables 1-8	1-4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 August 2016	11/08/2016

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

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/062827

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	TRICOLI V ET AL: "Ammonia selective hollow fibers", JOURNAL OF MEMBRANE SCIENCE, ELSEVIER BV, NL, vol. 104, no. 1, 15 August 1995 (1995-08-15), pages 19-26, XP004041319, ISSN: 0376-7388, DOI: 10.1016/0376-7388(94)00208-G table 1	1-4
Y	EP 0 130 846 A2 (FOSTER WHEELER ENERGY CORP [US]) 9 January 1985 (1985-01-09) page 2, lines 6-9; figures 1,2c page 4, lines 8-13 page 11, line 8 - page 12, line 26	5-7
X	US 5 455 016 A (CHOE JUN S [US] ET AL) 3 October 1995 (1995-10-03) cited in the application column 2, line 20 - column 3, line 25; figure 1	1-7

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2016/062827

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-7

Method and apparatus for making ammonia

1.1. claims: 1-4

Method for making ammonia comprising recycling product gas separated using condensing and membrane techniques, the membrane has a ammonia to hydrogen selectivity of at least 4.

1.2. claims: 5-7

Reactor for ammonia production comprising an ammonia converter, heat exchangers, a boiler, a preheater , a compressor and a membrane

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/062827

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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