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(54) **Method of removing nitrogen from a nitrogen containing stream**

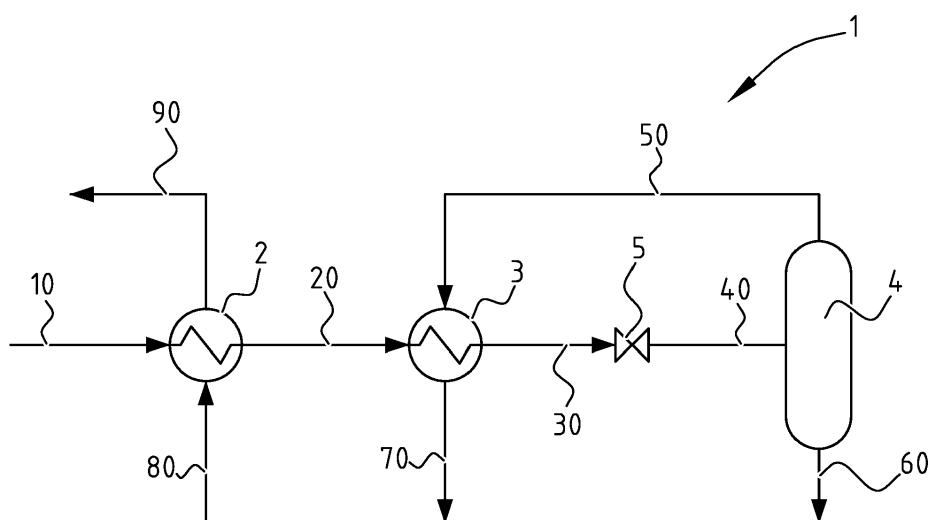
(57) The present invention provides a method of removing nitrogen from a nitrogen-containing stream (10), the method comprising at least the steps of:

- (a) providing a nitrogen-containing stream (10) having a pressure of at least 5.0 bara and a temperature of at most 20°C;
- (b) cooling the nitrogen-containing stream (10) in a first (2) and a second heat exchanger (3) thereby obtaining a cooled nitrogen-containing stream (30);
- (c) expanding the cooled nitrogen-containing stream (30)

thereby obtaining an expanded nitrogen-containing stream (40);

- (d) separating the expanded nitrogen-containing stream (40) in a gas/liquid separator (4) thereby obtaining a gaseous nitrogen-enriched stream (50) and a liquid nitrogen-depleted stream (60); and

- (e) heating the gaseous nitrogen-enriched stream (50) in the first or second heat exchanger (2,3) thereby obtaining a heated nitrogen-enriched stream (70).



**FIG. 1**

## Description

[0001] The present invention relates to a method of removing nitrogen from a nitrogen-containing stream.

[0002] Methods of removing nitrogen from a nitrogen-containing stream are known in the art. As an example, it is known to remove nitrogen using an NRU (Nitrogen Rejection Unit). A problem of using an NRU for removing nitrogen is the high expenditure associated with it.

[0003] It is an object of the present invention to solve or at least minimize the above problem.

[0004] It is a further object of the present invention to provide a simpler and more cost-effective method of removing nitrogen from a nitrogen-containing stream, in particular a methane-rich stream such as obtained during the liquefaction of natural gas.

[0005] One or more of the above or other objects are achieved according to the present invention by providing a method of removing nitrogen from a nitrogen-containing stream, the method comprising at least the steps of:

- (a) providing a nitrogen-containing stream having a pressure of at least 5.0 bara and a temperature of at most 20°C;
- (b) cooling the nitrogen-containing stream in a first and a second heat exchanger thereby obtaining a cooled nitrogen-containing stream;
- (c) expanding the cooled nitrogen-containing stream thereby obtaining an expanded nitrogen-containing stream;
- (d) separating the expanded nitrogen-containing stream in a gas/liquid separator thereby obtaining a gaseous nitrogen-enriched stream and a liquid nitrogen-depleted stream; and
- (e) heating the gaseous nitrogen-enriched stream in the first or second heat exchanger thereby obtaining a heated nitrogen-enriched stream.

[0006] An advantage of the method according to the present invention is that it has a surprisingly simple design and can be standardized to treat and liquefy a wide range of feed gas compositions. Further, there is relatively limited utility and chemicals requirement resulting in a significant OPEX and CAPEX reduction.

[0007] In step (a), a nitrogen-containing stream is provided. Although the nitrogen-containing stream is not particularly limited (other than having a pressure of at least 5.0 bara and a temperature of at most 20°C), it preferably is a methane-rich gas stream. Preferably, the nitrogen-containing stream comprises at least 5 mol% nitrogen, preferably at least 10 mol%, more preferably at least 12 mol%. Typically, the nitrogen-containing stream contains less than 80 mol% nitrogen. According to a preferred embodiment, the nitrogen-containing stream comprises at least 20 mol%, preferably at least 40 mol% methane, and typically below 85 mol%. Although the method according to the present invention is less critical (than usual) to C<sub>2+</sub> (the nitrogen-containing stream provided in step (a) may contain more than 0.2 mol% C<sub>2+</sub>), it is preferred that the nitrogen-containing stream comprises at most 2.0 mol% C<sub>2+</sub>, preferably at most 1.0 mol%, more preferably at most 0.5 mol%. In the context of the present invention, "C<sub>2+</sub>" refers to C<sub>2+</sub>-hydrocarbons, i.e. hydrocarbons containing 2 or more carbon atoms per molecule. Further it is preferred that the nitrogen-containing stream comprises at most 200 ppm CO<sub>2</sub>, preferably at most 100 ppm CO<sub>2</sub>, more preferably at most 50 ppm CO<sub>2</sub>.

[0008] As indicated above, the nitrogen-containing stream provided in step (a) has a pressure of above 5.0 bara (and preferably above 6.0 bara, more preferably above 10.0 bara). Preferably, the nitrogen-containing stream has a pressure of at most 30.0 bara, preferably at most 25 bara. Further, it is preferred that the nitrogen-containing stream has a temperature of at most (i.e. below) -50°C. Typically, the nitrogen-containing stream has a temperature of at least (i.e. above) -150°C, preferably at least -140°C, more preferably at least -125°C.

[0009] In step (b), the nitrogen-containing stream is cooled in a first and a second heat exchanger thereby obtaining a cooled nitrogen-containing stream. Preferably, in step (b) the nitrogen-containing stream is cooled first in the first heat exchanger and then in the second heat exchanger to obtain the cooled nitrogen-containing stream. Preferably, the cooled nitrogen-containing stream has a temperature of from -145°C to -155°C. Preferably, the nitrogen-containing stream is cooled in the first heat exchanger against a stream having a temperature of from -165°C to -110°C, preferably at least -160°C and preferably at most -150°C. The stream against which nitrogen-containing stream is cooled in the first heat exchanger typically has a temperature after heat exchanging of from -145°C to -45°C.

[0010] In step (c), the cooled second nitrogen-containing stream is expanded thereby obtaining an expanded nitrogen-containing stream. Although the expander as used in step (c) according to the present invention is not particularly limited (and may include a JT valve an orifice, a common expander, etc.), it is preferred that in the expander enthalpy is withdrawn from the cooled nitrogen-containing stream. A suitable expander for withdrawing enthalpy whilst expanding is a turboexpander.

[0011] Typically, the expanded nitrogen-containing stream has a pressure of from 1.5 to 6.0 bara, preferably about 2.0 bara. Preferably, the expanded nitrogen-containing stream obtained in step (c) has a temperature of at most -150°C, preferably at most -155°C, more preferably at most -160°C.

[0012] In step (d), the expanded nitrogen-containing stream is separated in a gas/liquid separator thereby obtaining a gaseous nitrogen-enriched stream and a liquid nitrogen-depleted stream. Preferably, the gaseous nitrogen-enriched

stream obtained in step (d) comprises from 30 to 75 mol% nitrogen, preferably above 40 mol%, more preferably above 50 mol% and preferably less than 70 mol%. Further it is preferred that the liquid nitrogen-depleted stream obtained in step (d) comprises at least 90 mol% methane, preferably at least 92 mol% and typically less than 98 mol%, preferably less than 95 mol%. Typically, the liquid nitrogen-depleted stream obtained in step (d) comprises less than 10 mol% nitrogen.

**[0013]** In step (e) the gaseous nitrogen-enriched stream is heated in the first or second heat exchanger thereby obtaining a heated nitrogen-enriched stream. Preferably, in step (e) the gaseous nitrogen-enriched stream is heated in the second heat exchanger.

**[0014]** Typically the heated nitrogen-enriched stream has a temperature of from -155°C to 30°C, preferably about 15°C. Further, the gaseous nitrogen-enriched stream typically has a pressure of from 1.5 to 6.0 bara.

**[0015]** Hereinafter the invention will be further illustrated by the following non-limiting drawing. Herein shows:

Fig. 1 schematically a process scheme for performing the method according to the present invention.

**[0016]** For the purpose of this description, same reference numbers refer to same or similar components.

**[0017]** Fig. 1 schematically shows a process scheme for performing a method of removing nitrogen from a nitrogen-containing stream. The process scheme is generally referred to with reference number 1.

**[0018]** The process scheme 1 comprises a heat exchanger 2 ("the first heat exchanger") and a heat exchanger 3 ("the second heat exchanger"), a gas/liquid separator 4 and JT-valve 5. The process scheme may comprise further heat exchangers in addition to the first heat exchanger 2 and second heat exchanger 3. Preferably, the first heat exchanger 2 and second heat exchanger 3 are separate heat exchangers.

**[0019]** During use of the process scheme 1 according to the present invention, a nitrogen-containing stream 10 is provided. Typically the nitrogen-containing stream 10 is a cold stream and originates from e.g. a gas/liquid separator running at relatively cold conditions. The nitrogen-containing stream 10 is cooled in the first and second heat exchangers 2,3 thereby obtaining a cooled nitrogen-containing stream 30. The first and second heat exchangers 2 and 3 are indirect heat exchangers; hence no direct contact between the streams takes place, but only heat exchanging contact. In the embodiment of Figure 1, the nitrogen-containing stream 10 is cooled first in the first heat exchanger 2 (against stream 80, resulting in heated stream 90) and then (as stream 20) in the second heat exchanger 3 to obtain the cooled nitrogen-containing stream 30.

**[0020]** Then, the cooled nitrogen-containing stream 30 is expanded in JT-valve 5 thereby obtaining an expanded nitrogen-containing stream 40, which stream 40 is separated in the gas/liquid separator 4 to obtain a gaseous nitrogen-enriched stream 50 and a liquid nitrogen-depleted stream 60. The gaseous nitrogen-enriched stream 50 is heated (in the embodiment of Figure 1) in the second heat exchanger 3 thereby obtaining a heated nitrogen-enriched stream 70. The heated nitrogen-enriched stream 70 may be sent to e.g. a duct (or auxiliary) burner of a gas turbine to be used as a fuel gas.

**[0021]** Stream 80 may originate from e.g. an LNG end flash system and heated stream 90 (obtained after heat exchanging stream 80 against stream 10 in the first heat exchanger 2) may be sent to e.g. a loop and recycled.

### Examples

**[0022]** Tables 1 and 2 below show two actual non-limiting examples of the method according to the present invention, providing information on conditions and composition of the various streams, whilst using the scheme of Figure 1 for removing nitrogen from a nitrogen-containing stream. In the example of Table 1, the nitrogen-containing stream was provided at a lower temperature (-115.0°C) than that of Table 2 (-60.2°C).

### Example 1

**[0023]**

Table 1. Composition and properties of various streams

Stream	Pressure [bara]	Temp. [°C]	State	CH <sub>4</sub> [mol%]	N <sub>2</sub> [mol%]	C <sub>2+</sub> [mol%]
10	14.7	-115.0	Gas	84.7	15.0	0.3
20	14.5	-150.5	Gas	84.7	15.0	0.3
30	14.3	-151.4	Gas	84.7	15.0	0.3
40	2.3	-163.8	Gas/liquid	84.7	15.0	0.3

(continued)

Stream	Pressure [bara]	Temp. [°C]	State	CH <sub>4</sub> [mol%]	N <sub>2</sub> [mol%]	C <sub>2+</sub> [mol%]
50	2.3	-163.8	Gas	36.0	64.0	-
60	2.3	-163.8	Liquid	92.5	7.2	0.3
70	2.1	-152.5	Gas	36.0	64.0	-
80	1.05	-162.6	Gas	83.7	16.3	-
90	0.85	-117.4	Gas	83.7	16.3	-

Example 2**[0024]**Table 2. Composition and properties of various streams

Stream	Pressure [bara]	Temp. [°C]	State	CH <sub>4</sub> [mol%]	N <sub>2</sub> [mol%]	C <sub>2+</sub> [mol%]
10	14.4	-60.2	Gas	84.8	14.9	0.3
20	14.2	-150.5	Gas	84.8	14.9	0.3
30	14.0	-151.4	Gas	84.8	14.9	0.3
40	2.3	-163.9	Gas/liquid	84.8	14.9	0.3
50	2.3	-163.9	Gas	35.9	64.1	-
60	2.3	-163.9	Liquid	92.5	7.2	0.3
70	2.1	-152.5	Gas	35.9	64.1	-
80	1.05	-162.7	Gas	83.3	16.7	-
90	0.85	-104.8	Gas	83.3	16.7	-

Discussion

**[0025]** As can be seen from Tables 1 and 2, the present invention allows for an effective removal of nitrogen (via stream 50/70) from stream 10. Stream 60 contained only 7.2 mol% N<sub>2</sub>.

**[0026]** The person skilled in the art will readily understand that many modifications may be made without departing from the scope of the invention.

**Claims**

1. A method of removing nitrogen from a nitrogen-containing stream (10), the method comprising at least the steps of:

- (a) providing a nitrogen-containing stream (10) having a pressure of at least 5.0 bara and a temperature of at most 20°C;
- (b) cooling the nitrogen-containing stream (10) in a first (2) and a second heat exchanger (3) thereby obtaining a cooled nitrogen-containing stream (30);
- (c) expanding the cooled nitrogen-containing stream (30) thereby obtaining an expanded nitrogen-containing stream (40);
- (d) separating the expanded nitrogen-containing stream (40) in a gas/liquid separator (4) thereby obtaining a gaseous nitrogen-enriched stream (50) and a liquid nitrogen-depleted stream (60); and
- (e) heating the gaseous nitrogen-enriched stream (50) in the first or second heat exchanger (2,3) thereby obtaining a heated nitrogen-enriched stream (70).

2. The method according to claim 1, wherein the nitrogen-containing stream (10) in step (a) comprises at least 5 mol% nitrogen, preferably at least 10 mol%, more preferably at least 12 mol%.

3. The method according to claim 1 or 2, wherein the nitrogen-containing stream (10) comprises at most 2.0 mol% C<sub>2+</sub>, preferably at most 1.0 mol%, more preferably at most 0.5 mol%.
4. The method according to any one of claims 1-3, wherein the nitrogen-containing stream (10) comprises at most 100 ppm CO<sub>2</sub>, preferably at most 100 ppm CO<sub>2</sub>, more preferably at most 50 ppm CO<sub>2</sub>.
5. The method according to any one of claims 1-4, wherein the nitrogen-containing stream (10) has a pressure of at most 30 bara, preferably at most 25 bara.
6. The method according to any one of claims 1-5, wherein the nitrogen-containing stream (10) has a temperature of at most -50°C.
7. The method according to any one of claims 1-6, wherein in step (b) the nitrogen-containing stream (10) is cooled first in the first heat exchanger (2) and then in the second heat exchanger (3) to obtain the cooled nitrogen-containing stream (30).
8. The method according to claim 7, wherein the nitrogen-containing stream (10) is cooled in the first heat exchanger (2) against a stream (80) having a temperature of from -165°C to -110°C, preferably at least -160°C and preferably at most -150°C.
9. The method according to any one of claims 1-8, wherein the expanded nitrogen-containing stream (40) obtained in step (c) has a temperature of at most -150°C, preferably at most -160°C, more preferably at most -165°C.
10. The method according to any one of claims 1-9, wherein the gaseous nitrogen-enriched stream (50) obtained in step (d) comprises from 30 to 75 mol% nitrogen, preferably above 40 mol%, more preferably above 50 mol% and preferably less than 70 mol%.
11. The method according to any one of claims 1-10, wherein the liquid nitrogen-depleted stream (60) obtained in step (d) comprises at least 90 mol% methane, preferably at least 92 mol%.
12. The method according to any one of claims 1-11, wherein in step (e) the gaseous nitrogen-enriched stream (50) is heated in the second heat exchanger (3).

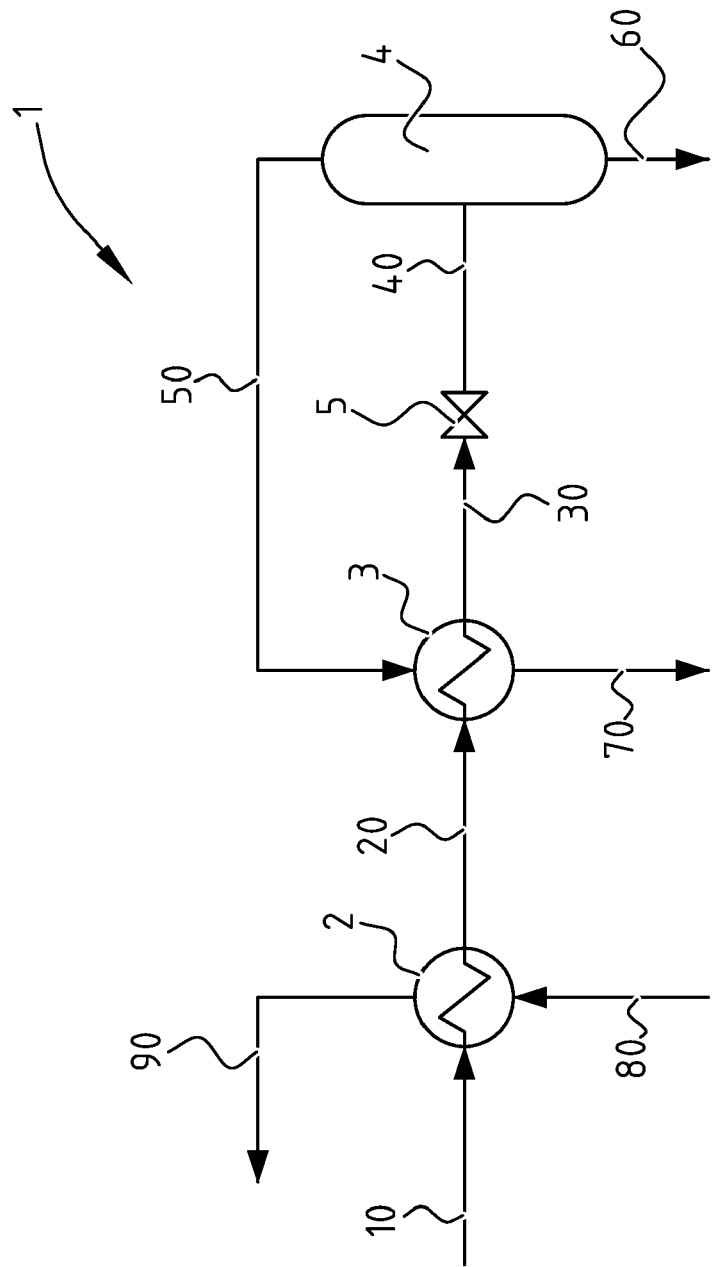


FIG. 1



## EUROPEAN SEARCH REPORT

Application Number  
EP 15 15 0824

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 160 489 A (JACK BROCOFF ET AL) 8 December 1964 (1964-12-08) * column 2, lines 40-41 * * column 3, lines 58-66 * * column 4, lines 5-9; figure *	1-12	INV. F25J3/06 F25J1/00
X	US 3 360 944 A (HELMUT KNAPP ET AL) 2 January 1968 (1968-01-02) * column 1, lines 63-68; figure 1 * * column 2, line 43 - column 3, line 8 *	1-12	
X	US 2003/136146 A1 (FISCHER-CALDERON ERNESTO [US] ET AL) 24 July 2003 (2003-07-24) * paragraphs [0063], [0075], [0076], [0078], [0079]; figure 3 *	1-12	
			TECHNICAL FIELDS SEARCHED (IPC)
			F25J
The present search report has been drawn up for all claims			
Place of search <b>Munich</b>		Date of completion of the search <b>13 July 2015</b>	Examiner <b>Göritz, Dirk</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 15 15 0824

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13-07-2015

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3160489 A	08-12-1964	NONE	
US 3360944 A	02-01-1968	AT 277179 B DD 71567 A1 DE 1551597 A1 ES 338696 A1 FR 1517491 A GB 1115689 A US 3360944 A	10-12-1969 05-03-1970 23-04-1970 01-04-1968 15-03-1968 29-05-1968 02-01-1968
US 2003136146 A1	24-07-2003	AU 2002351361 B2 CA 2470234 A1 CN 1615422 A EG 24209 A EP 1468231 A1 MX PA04006770 A NO 20034141 A US 2003136146 A1 WO 03062724 A1	05-06-2008 31-07-2003 11-05-2005 23-10-2008 20-10-2004 10-11-2004 17-11-2003 24-07-2003 31-07-2003

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