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(54) **Method and device for completely condensing a process gas by cryocondensation**

(57) The present invention relates to a method and a device for completely condensing a process gas (P) by cryocondensation, comprising the following steps: cooling a gaseous cooling medium circulating in a cooling loop (10) by a liquid cooling medium in a main heat exchanger (11), whereby vaporizing the liquid cooling medium, feeding the vaporized cooling medium into the cooling loop (10) upstream of the main heat exchanger (11), cooling heat exchange surfaces (5) in a condenser (3) by the gaseous cooling medium circulating in the cooling loop (10), feeding the process gas (P) to be condensed into the condenser (3) to bring it into contact with the heat exchange surfaces (5) in the condenser (3), collecting the condensed process gas (P) as liquid product (LP) in a product container (8), and extracting gaseous cooling medium by an extractor (16) from the cooling loop

(10) and guiding it through a pre-cooler (2) for pre-cooling the process gas (P) before feeding it into the condenser (3). The invention allows to completely condensate a process gas (P) by using the cold of a liquid cooling medium in three steps. In a main heat exchanger (11) the phase transfer from liquid to gas is used. In a second step the still very cold gas is introduced into the cooling loop (10), and in a final step the temperature difference between the cooling loop (10) after the heat exchange surfaces (5) in the condenser (3) compared to the environment (25) is mostly used in a pre-cooler (2). This highly efficient use of the cold allows using the process and the device according to the invention on an industrial scale for completely condensing a process gas (P).

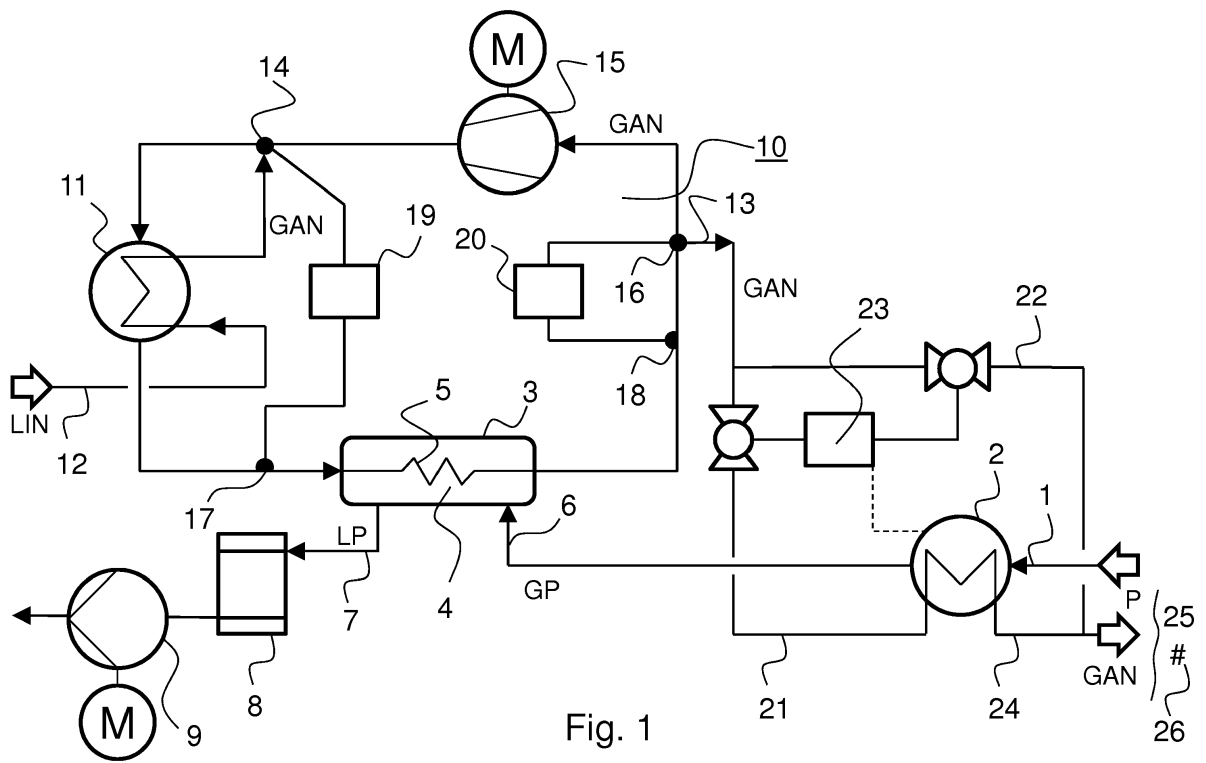


Fig. 1

Description

[0001] The present invention relates to a process and a device for completely condensing a process gas by cryocondensation.

[0002] The principle of cryocondensation is well known for processes to clean a process gas from undesired components, which can be condensed to be separated from the process gas to be cleaned. Details of such a method and a corresponding device are for example disclosed in WO 2008/7055804 A1. In most cases the cleaning of process gas from undesired components is directed to very small amounts of gas to be condensed and the focus for such devices is not mainly directed to economic aspects how to make the condensation of very small amounts highly efficient concerning energy consumption.

[0003] For industrial purposes it is also known to convert a process gas by cryocondensation completely into a liquid product. As, in this case, cryocondensation has to compete with other methods for liquefying gases, for economic reasons, liquid nitrogen is mainly as cooling medium for cryocondensation economic reasons. For this reason, the invention is described in the following mainly with reference to nitrogen as cooling medium. However, in special cases, other gases can be used as cooling medium if they are available in liquid phase at the right temperature and can be used afterwards in gaseous phase under economic conditions.

[0004] It is an object of the present invention to provide an improved method for completely liquefying a process gas by cryocondensation, and in particular to make the method highly efficient. Another object of the present invention is to provide a device for carrying out such a method.

[0005] The solutions for the described objects are given by a method according to independent claim 1 and a device according to independent claim 6. Advantageous features, which can be combined with each other in different ways, are described in the respective dependent claims.

[0006] The present invention relates to a method for completely condensing a process gas by cryocondensation, comprising the following steps:

- Cooling gaseous nitrogen or another cooling medium circulating in a cooling loop by liquid nitrogen or the other cooling medium in liquid phase, respectively, in a main heat exchanger, whereby vaporizing the cooling medium, in particular the liquid nitrogen,
- feeding the vaporized cooling medium into the cooling loop upstream of the main heat exchanger,
- cooling the heat exchange surfaces in a condenser by the gaseous cooling medium or nitrogen circulating in the cooling loop,
- feeding the process gas to be condensed into the condenser to bring it into contact with the heat exchange surfaces in the condenser,

- collecting the condensed process gas as liquid product in a product container,
- extracting gaseous cooling medium, in particular nitrogen, by an extractor from the cooling loop and guiding it through a pre-cooler for pre-cooling the process gas before feeding the process gas into the condenser.

[0007] The method according to the invention uses liquid nitrogen or another cooling medium at three different stages to contribute to the cooling down and liquefying a process gas. In a first step the gaseous nitrogen circulating in the cooling loop is cooled in the main heat exchanger with liquid nitrogen, whereby the liquid nitrogen is vaporized. This means that the main heat exchanger should be designed to allow the liquid nitrogen to be completely vaporized during the heat exchange, resulting in a sharp decrease of the temperature of the gaseous nitrogen in the cooling loop. In a next step the still very cold, but completely vaporized nitrogen is introduced into the cooling loop, thereby further lowering the temperature in the cooling loop. Finally, part of the gaseous nitrogen circulating in the cooling loop and still being cold is extracted from the cooling loop to be used a third time in the pre-cooler to pre-cool the process gas before the latter enters the condenser. Thereafter, the gaseous cooling medium can be released into the environment or can be used in an industrial network distributing the cooling medium, in particular nitrogen. The chain for using the cold of liquid medium/nitrogen in the process allows using almost the whole cold in liquid nitrogen up to the stage where the medium/nitrogen is at ambient pressure and temperature.

[0008] An important advantage of the present invention is that the pre-cooler takes over a part of the cooling of the process gas. This allows to keep the temperature in the condenser in a range, which avoids freezing of the process gas at certain areas of the heat exchange surfaces. The temperature in all areas of the condenser can be maintained above the freezing temperature of the process gas so as to maintain a stable condensing process, which does not require any deicing from time to time. The use of nitrogen as cooling medium allows keeping the condenser temperature between the dew point and the freezing temperature of many gases, for which such cryocondensation according to the invention can be used, for example Ethylene, Argon, Propene, LNG, Butadiene, Dichloride-Methane, Styrene, or Formaldehyde.

[0009] To make the process stable and to allow reacting on different amounts of process gas being supplied to the condenser it is advantageous to control the temperature in the cooling loop upstream of the condenser and to regulate the flow of liquid nitrogen through the main heat exchanger and the subsequent feeding of gaseous nitrogen into the cooling loop in dependency of this temperature.

[0010] When feeding additional gaseous nitrogen into the cooling loop it is also advantageous to control the

pressure in the cooling loop, what is done according to another feature of the invention by measuring the pressure in the cooling loop and by controlling the volume per time of gaseous nitrogen extracted from the cooling loop in dependency of this pressure. This allows to keep the pressure in the cooling loop constant or to vary it according to the needs of the process, by controlling the amount of cooling medium (for example expressed in terms of normal volume) circulating in the cooling loop.

[0011] Under certain circumstances it can happen that not all nitrogen extracted from the cooling loop should be used in the pre-cooler, in particular to avoid that the temperature in the pre-cooler drops below the condensation temperature of the process gas. In this case it is possible to feed the extracted nitrogen at least partly into a by-pass line by-passing the pre-cooler before it is released to the environment or to an industrial network.

[0012] If required in function of variable amounts of process gas to be condensed, a distribution controller can be used to distribute the extracted nitrogen to the pre-cooler and the by-pass line, in particular depending on the cooling required in the pre-cooler. The value measured by a temperature sensor in the pre-cooler, in particular at the outlet of the pre-cooler, may be used to control the distribution of the extracted nitrogen by said distribution controller.

[0013] The invention also relates to a device for completely condensing a process gas, the device comprising:

- an inlet for the process gas,
- a pre-cooler for pre-cooling the process gas,
- a condenser with a condensing chamber,
- heat exchange surfaces in the condensing chamber,
- a condenser inlet to introduce pre-cooled process gas,
- a condenser outlet to extract liquefied process gas,
- a cooling loop for circulating gaseous cooling medium, in particular gaseous nitrogen, and for supplying said gaseous cooling medium to the condensing chamber for cooling the heat exchange surfaces,
- a main heat exchanger in the cooling loop for cooling the gaseous cooling medium with liquid cooling medium, in particular liquid nitrogen, thereby vaporizing the liquid cooling medium,
- a feeder for feeding the vaporized cooling medium from the main heat exchanger into the cooling loop,
- an extractor for extracting gaseous cooling medium from the cooling loop,
- a pre-cooling line to feed the extracted gaseous cooling medium into the pre-cooler,
- a cooling medium outlet for releasing cooling medium, in particular nitrogen, into the environment and/or to an industrial network, said cooling medium outlet being connected to the pre-cooler so as to receive gaseous cooling medium therefrom.

[0014] The device according to the invention allows with simple equipment and tubing to use liquid nitrogen

in a highly efficient way to completely condense a process gas by cryocondensation.

[0015] In a further embodiment of the present invention there is a by-pass line for guiding nitrogen from the extractor by-passing the pre-cooler to the nitrogen outlet. This by-pass line allows making the nitrogen flow through the pre-cooler independent of the amount of nitrogen extracted from the cooling loop to keep the temperature in the pre-cooler in a desired range.

[0016] Another embodiment of the invention comprises a temperature sensor in the cooling loop upstream of the condenser, which is connected to a temperature controller for controlling the amount of liquid nitrogen flowing through the main heat exchanger, which feature allows to keep the temperature in the cooling loop constant or to adapt it to the varying requirements of the process, in particular when different amounts of process gas or process gas with a different initial temperature are introduced into the system.

[0017] Yet another embodiment of the invention comprises a pressure sensor in the cooling loop connected to a pressure controller for controlling the pressure in the cooling loop, in particular by controlling the volume per time of nitrogen extracted by the extractor. This feature allows to keep the pressure in the cooling loop constant or to adapt it to certain requirements of the process, by controlling the amount of nitrogen circulating in the cooling loop. Moreover, it is a safety feature to avoid any overpressure in the cooling loop and its components.

[0018] To allow extracting nitrogen from the cooling loop independent of the cool required in the pre-cooler there is in another embodiment of the invention a distribution controlling means to distribute the extracted nitrogen on the pre-cooler and the by-pass line depending on the required cooling in the pre-cooler.

[0019] Additional details of the invention are explained with regard to the drawing, which shows an embodiment of the invention. However, the invention is not restricted to this embodiment and the shown components can be used in different combinations with each other or with other known components. It should also be noted that the shown example is described with nitrogen as cooling medium. However, another gas may be used as cooling medium according to the invention.

[0020] Fig. 1 shows a schematic embodiment of a device for condensing a process gas according to the invention.

[0021] A process gas P is supplied to an inlet 1 and then guided through a pre-cooler 2 to a condenser 3. The still gaseous process gas GP enters the condenser 3 through a condenser inlet 6. In a condensing chamber 4 the gaseous process gas GP comes into contact with heat exchange surfaces 5 such that it is completely condensed. The resulting liquid product LP leaves the condensing chamber 4 through a condenser outlet 7 and is collected in a product container 8. From the product container 8 it can be pumped by a transport pump 9 to any point of further use or component.

[0022] The heat exchange surfaces 5 in the condensing chamber 4 are cooled by a cooling loop 10, in which gaseous nitrogen GAS is circulated as cooling medium.

[0023] A main heat exchanger 11 in the cooling loop 10 is used to cool down the circulating nitrogen GAS by feeding liquid nitrogen LIN through an inlet 12 for liquid nitrogen, into the main heat exchanger 11. The liquid nitrogen LIN is vaporized in the main heat exchanger 11. The resulting gaseous nitrogen is fed by a feeder 14 into the cooling loop 10 upstream of the main heat exchanger 10, whereby cooling down the nitrogen in the cooling loop 10. A circulation pump 15 transports the gaseous nitrogen GAN in the cooling loop 10 following the direction as symbolized by arrows through the main heat exchanger 11 to the condenser 3, where it flows through the heat exchange surfaces 5, and then to an extractor 16, which extracts some of the gaseous nitrogen GAN from the cooling loop 10. The extracted gaseous nitrogen GAN flows through a loop outlet 13 and a pre-cooling line 21 to the pre-cooler 2. Finally, the gaseous nitrogen GAS is guided to a cooling medium/nitrogen outlet 24 where it is released to the environment 25 or to an industrial network 26, in which it can be used for other purposes.

[0024] For controlling the temperature in the cooling loop 10 and especially at the inlet to the heat exchange surfaces 5 there is a temperature sensor 17 in the cooling loop 10. This temperature sensor 17 is connected to a temperature controller 19, which controls the feeder 14 and more specifically the amount of liquid nitrogen LIN fed into the cooling loop through inlet 12 for liquid nitrogen. The cooling loop 10 also comprises a pressure sensor 18 connected to a pressure controller 20, which controls the extractor 16 so as to keep the pressure in the cooling loop 10 constant, in a desired range or at a desired level in function of the cooling requirements in the condenser 3. If not all of the extracted gaseous nitrogen GAN at the loop outlet 13 for gaseous nitrogen can be used in the pre-cooler 2, part of it can be guided through a by-pass line 22 by-passing the pre-cooler 2 to the cooling medium/nitrogen outlet 24. A distribution controller 23 controlling appropriate valves in the pre-cooling line 21 and the by-pass line 22 allows distributing the nitrogen flow on both lines depending on the cooling required in the pre-cooler 2.

[0025] The present invention allows to completely condensate a process gas by using the cold of liquid nitrogen in three steps. In a main heat exchanger the phase change from liquid to gas is used. In a second step the still very cold gas is introduced into the cooling loop, and in a final step the temperature difference between the cooling loop 10 after the heat exchange surfaces 5 in the condenser 3 compared to the environment is mostly used in a pre-cooler. This highly efficient use of the cold allows using the process and the device according to the invention on an industrial scale for completely condensing a process gas.

[0026] The present invention is particularly useful for the complete condensation of so-called "clean" process

gases. A clean process gas in the sense of the present invention refers to a process gas which either contains only one chemical component or which is a mixture of chemical components substantially without undesired impurities and having similar condensation points, for example between -180 and 0° C, in particular the condensation points all being in an interval of 20 to 50° C in the above temperature range, so that the mixture can be fully condensed in a single step by condensing it on a cold surface having a temperature below the condensation point or a range of condensation points of the process gas at a given pressure, especially at atmospheric pressure.

Reference List

[0027]

1	inlet for process gas
2	pre-cooler
3	condenser
4	condensing chamber
5	heat exchange surfaces
6	condenser inlet
7	condenser outlet
8	product container
9	transport pump
10	cooling loop
11	main heat exchanger
12	inlet for liquid cooling medium/nitrogen
13	loop outlet
14	feeder
15	circulation pump
16	extractor
17	temperature sensor
18	pressure sensor
19	temperature controller
20	pressure controller
21	pre-cooling line
22	by-pass line
23	distribution controller
24	cooling medium/nitrogen outlet
25	environment
26	industrial network
LIN	liquid nitrogen
GAN	gaseous nitrogen
P	process gas
GP	gaseous process gas
LP	liquid product

Claims

- Method for completely condensing a process gas (P) by crycondensation with a gaseous cooling medium, in particular gaseous nitrogen (GAN), the method comprising the following steps:

- circulating the gaseous cooling medium in a cooling loop (10),
 - cooling the gaseous cooling medium with a liquid cooling medium, in particular liquid nitrogen (LIN), in a main heat exchanger (11), thereby vaporizing the liquid cooling medium,
 - feeding the vaporized cooling medium into the cooling loop (10) upstream of the main heat exchanger (11),
 - cooling heat exchange surfaces (5) in a condenser (3) with the gaseous cooling medium, in particular gaseous nitrogen (GAN), circulating in the cooling loop (10),
 - feeding the process gas (P) to be condensed into the condenser (3) to bring it into contact with the cooled heat exchange surfaces (5) in the condenser (3),
 - collecting the condensed process gas (P) as liquid product (LP) in a product container (8),
 - extracting gaseous cooling medium by an extractor (16) from the cooling loop (10) and guiding at least part of the extracted gaseous cooling medium through a pre-cooler (2) for pre-cooling the process gas (P) before feeding the pre-cooled process gas into the condenser (3).
2. Method according to claim 1, wherein the amount of liquid cooling medium flowing through the main heat exchanger (11) and fed after vaporization into the cooling loop (10) is controlled in dependency of a temperature in the cooling loop upstream of the condenser (3).
 3. Method according to claim 1 or 2, wherein the volume of gaseous cooling medium extracted from the cooling loop (10) is controlled in dependency of the pressure in the cooling loop (10), especially to keep the pressure in the cooling loop (10) constant.
 4. Method according to one of the preceding claims, wherein the extracted cooling medium can be fed into the pre-cooler (2) and/or into a by-pass line (21) by-passing the pre-cooler (2) in dependency of the cooling required in the pre-cooler (2) and wherein the nitrogen is finally released into the environment and/or into an industrial network (26).
 5. Method according to one of the preceding claims, wherein the distribution of the extracted cooling medium between the pre-cooler (2) and the by-pass line (22) is controlled by a distribution controller (23), in particular depending on the temperature in the pre-cooler (2).
 6. Device for completely condensing a process gas (P), the device comprising:
 - an inlet (1) for the process gas (P),
 - a pre-cooler (2) for pre-cooling the process gas (P),
 - a condenser (3) with a condensing chamber (4),
 - heat exchange surfaces (5) in the condensing chamber (4),
 - a condenser inlet (6) to introduce pre-cooled process gas (P) in the condenser (3),
 - a condenser outlet (7) to extract liquefied process gas (P) from the condenser (3),
 - a cooling loop (10) for circulating gaseous cooling medium, in particular gaseous nitrogen (GAN), and for supplying the gaseous cooling medium to the condensing chamber (4) for cooling the heat exchange surfaces (5),
 - a main heat exchanger (11) in the cooling loop (10) for cooling the gaseous cooling medium with liquid cooling medium, in particular nitrogen (LIN), thereby vaporizing the cooling medium,
 - a feeder (14) for feeding the vaporized cooling medium from the main heat exchanger (11) into the cooling loop (10),
 - an extractor (16) for extracting gaseous cooling medium from the cooling loop (10),
 - a pre-cooling line (21) to feed the extracted gaseous cooling medium into the pre-cooler (2),
 - a cooling medium outlet (24) connected to the pre-cooler (2) to release gaseous cooling medium, in particular nitrogen, into the environment and/or an industrial network (26).
 7. Device according to claim 6, further comprising a by-pass line (22) for guiding gaseous cooling medium from the extractor (16) by-passing the pre-cooler (3) to the cooling medium outlet (24).
 8. Device according to claim 6 or 7, further comprising a temperature sensor (17) in the cooling loop (10) upstream of the condenser (3), the temperature sensor (17) being connected to a temperature controller (19) for controlling the amount of liquid cooling medium, in particular nitrogen (LIN), flowing through the main heat exchanger (11).
 9. Device according to one of the claims 6 to 8, further comprising a pressure sensor (18) in the cooling loop (10), the pressure sensor (18) being connected to a pressure controller (20) for controlling the pressure in the cooling loop (10), in particular by controlling the volume of gaseous cooling medium extracted from the cooling loop (10) by the extractor (16).
 10. Device according to one of the claims 7 to 9, comprising a distribution controller (23) for controlling the distribution of the extracted gaseous cooling medium between the pre-cooler (2) and the by-pass line (22), preferably depending on the required cooling in the pre-cooler (2).

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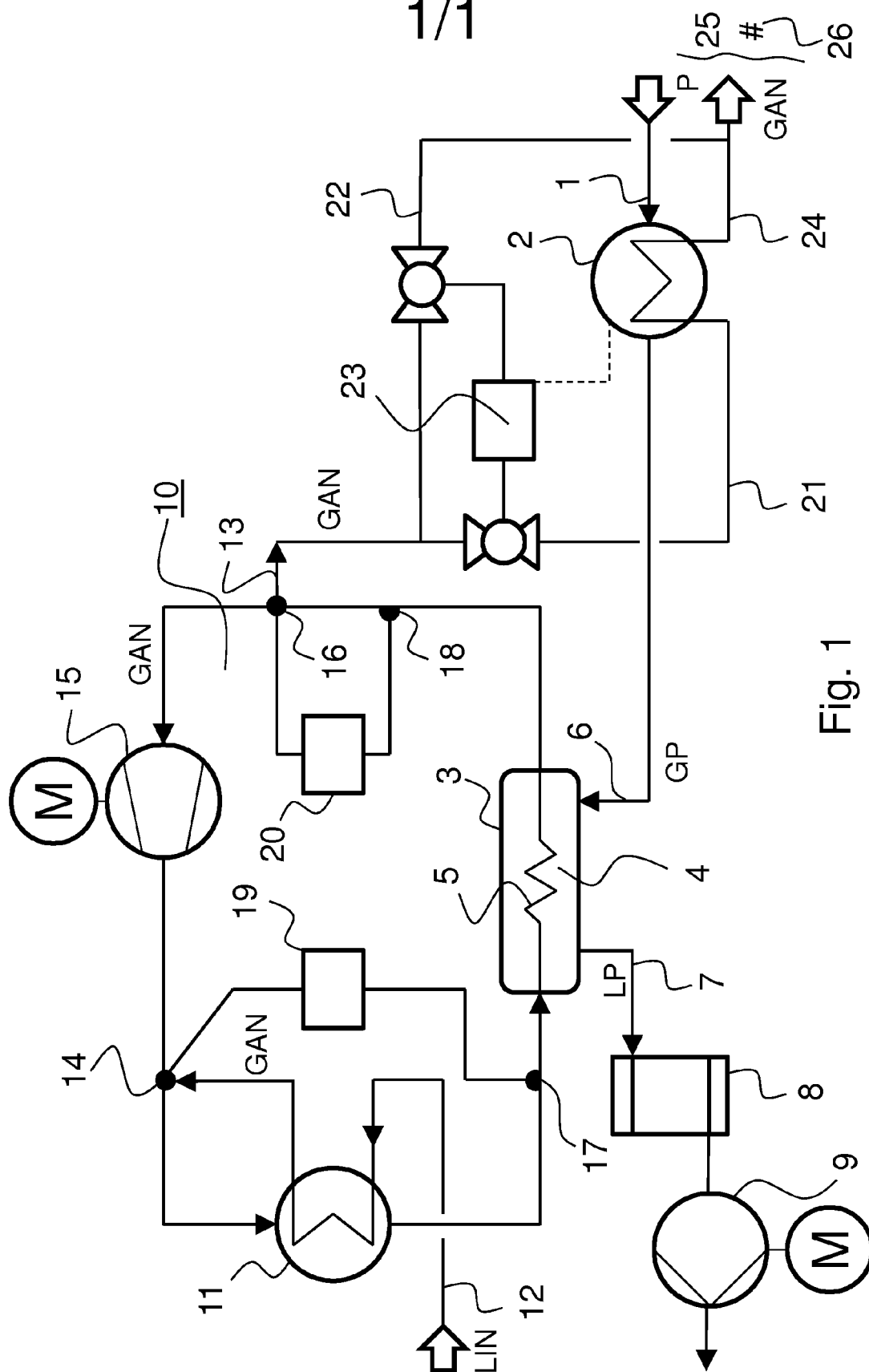


Fig. 1



EUROPEAN SEARCH REPORT

Application Number
EP 14 19 4689

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EPO FORM 1503 03.82 (P04C01)

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 4 141 707 A (SPRINGMANN HELMUT) 27 February 1979 (1979-02-27) * column 1, line 5 - column 1, line 13; figure 1 * * column 2, line 45 - column 3, line 45 *	1-3	INV. F25J1/00 F25J1/02 B01D5/00
A	ANONYMOUS: "Unit for the Recovery and Storage of Oxygen (URASO)", IP.COM JOURNAL, IP.COM INC., WEST HENRIETTA, NY, US, 15 March 2004 (2004-03-15), XP013014686, ISSN: 1533-0001 * page 2 - page 2; figure 2 *	1-10	
A	WO 2009/080678 A2 (SHELL INT RESEARCH [NL]; CHANTANT FRANCOIS [NL]; ELION WIVEKA JACOB A []) 2 July 2009 (2009-07-02) * page 16, line 11 - page 17, line 5; figure 4 *	1-10	
A	EP 1 944 074 A1 (LINDE AG [DE]) 16 July 2008 (2008-07-16) * paragraph [0001] - paragraph [0001]; figure 1 * * paragraph [0010] - paragraph [0010] * * paragraph [0012] - paragraph [0012] * * paragraph [0026] - paragraph [0030] *	1-10	TECHNICAL FIELDS SEARCHED (IPC) F25J
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 7 May 2015	Examiner Petereit, A
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			

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ON EUROPEAN PATENT APPLICATION NO.**

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07-05-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4141707 A	27-02-1979	DE 2631134 A1 US 4141707 A	19-01-1978 27-02-1979
-----	-----	-----	-----
WO 2009080678 A2	02-07-2009	CA 2707451 A1 CN 102124290 A EP 2225516 A2 JP 2011526993 A KR 20100098705 A US 2010319361 A1 WO 2009080678 A2	02-07-2009 13-07-2011 08-09-2010 20-10-2011 08-09-2010 23-12-2010 02-07-2009
-----	-----	-----	-----
EP 1944074 A1	16-07-2008	DE 102007001658 A1 EP 1944074 A1 US 2008202160 A1	17-07-2008 16-07-2008 28-08-2008
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 20087055804 A1 [0002]