



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
22.03.2017 Bulletin 2017/12

(51) Int Cl.:
F25J 3/04 (2006.01)

(21) Application number: **15185769.5**

(22) Date of filing: **18.09.2015**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

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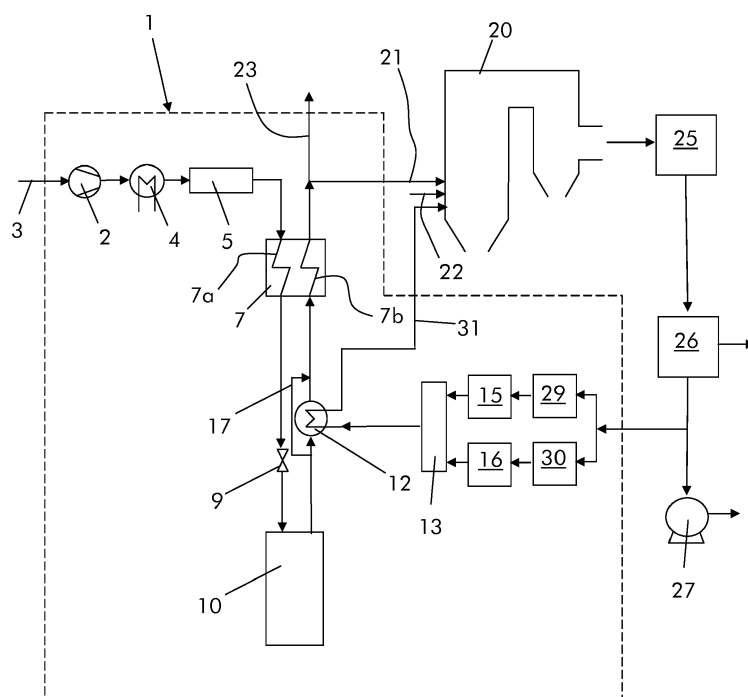
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(54) **CRYOGENIC UNIT AND METHOD FOR OPERATING A CRYOGENIC UNIT**

(57) The cryogenic unit (1) for gas treatment comprises a heat exchanger (7) having a first side (7a) and a second side (7b), an expansion valve (9) connected downstream of the first side (7a) of the heat exchanger (7), a gas treatment device (10) connected downstream of the expansion valve (9) and upstream of the second

side (7b) of the heat exchanger (7), at least an additional heat exchanger (12), a mixing device (13) connected to the at least an additional heat exchanger (12), a supply of a liquid connected to the mixing device (13), a supply of dry ice connected to the mixing device (13).

Fig. 2



Description

TECHNICAL FIELD

[0001] The present invention relates to a cryogenic unit and method for operating a cryogenic unit.

[0002] The cryogenic unit is for example part of an air separation unit (ASU) to produce oxygen from air or it can be part of a gas processing (GPU) unit in which flue gas is compressed and cooled in order to separate carbon dioxide from other gas. The cryogenic unit can further be used in an air separation unit and/or gas processing unit of a power plant for electric power generation and/or steam generation and/ or gasification plant.

BACKGROUND

[0003] Cryogenic units often have a compressor followed by a heat exchanger with a first warm side and a second cold side. A gas being treated is passed through the warm side of the heat exchanger and is cooled; the cooled gas being treated is thus expanded in an expansion valve to be further cooled and is then supplied into a gas separation device.

[0004] The treated gas discharged from the gas separation device is passed through the cold side of the heat exchanger, in order to cool the gas being treated passing through the warm side of the heat exchanger, and is then forwarded to further treatments.

[0005] Since cooling is achieved by expansion of the gas being treated in the expansion valve, at start-up it takes usually a long time to reach the operating temperature at the heat exchanger, i.e. for the gas being treated to be cooled at the heat exchanger to the required design temperature.

[0006] As an example, if the cryogenic unit described above is part of an air separation unit (ASU) of e.g. an oxygen fired power plant, it could take up to two days from start up to reach the operating temperature (between -160/-190°C) at the outlet of the heat exchanger (i.e. for the air cooled at the heat exchanger to have a temperature in the range -160/-190°C at the outlet of the heat exchanger).

[0007] The inventor has found a way to shorten the start-up time.

SUMMARY

[0008] An aspect of the invention includes providing a cryogenic unit and a method by which the start-up time can be reduced compared to what currently needed.

[0009] These and further aspects are attained by providing a cryogenic unit and a method in accordance with the accompanying claims.

[0010] Advantageously the flexibility of operation of the cryogenic unit can be increased according to the invention, because the additional heat exchanger provides increased flexibility to control the temperature of the gas

being treated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Further characteristics and advantages will be more apparent from the description of a preferred but non-exclusive embodiment of the cryogenic unit and method, illustrated by way of non-limiting example in the accompanying drawings, in which:

Figures 1 and 2 show different embodiments of a cryogenic unit being part of a power plant for electric power generation and/or steam generation; the cryogenic unit implements an air separation unit in these examples;

Figure 3 shows an embodiment of a cryogenic unit being part of a power plant for electric power generation and/or steam generation; the cryogenic unit implements a gas processing unit in this example.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0012] With reference to the figures, these show a cryogenic unit 1 for gas treatment.

[0013] The cryogenic unit is e.g. part of a power plant for electric power generation and/or steam generation and/or gasification plant such as IGCC. The power plant is preferably an oxyfuel power plant, i.e. a power plant having a boiler in which a fuel such as coal or oil, is burned in the presence of oxygen or oxygen enriched gas or substantially pure oxygen and recirculated flue gas. Use of the cryogenic unit of the invention in an oxyfuel power plant is advantageous, because in an oxyfuel power plant an air separation unit for separating oxygen from other gas constituting the air and a gas processing unit for separating carbon dioxide from other gas constituting the flue gas are needed; air separation unit and gas processing unit can thus advantageously implement the invention.

[0014] The cryogenic unit 1 can comprise a compressor 2 for compressing the gas being treated 3 and a heat exchanger 4, to remove the compression heat from the gas being treated.

[0015] The cryogenic unit 1 further has a cleaning system 5, such as a filter for dust removal and/or molar sieves for carbon dioxide and/or moisture removal by adsorption.

[0016] The cryogenic unit 1 further includes a heat exchanger 7 having a first side 7a and a second side 7b; an expansion valve 9 is connected downstream of the first side 7a of the heat exchanger 7 and a gas treatment device 10 is connected downstream of the expansion valve 9 and upstream of the second side 7b of the heat exchanger 7.

[0017] The cryogenic unit 1 further has at least an additional heat exchanger 12. Bypasses 17 can be provided in parallel to the heat exchangers 12.

[0018] The additional heat exchangers 12 can be provided in different positions of the cryogenic unit 1 and are used to provide additional cooling to the gas being treated, in addition to the cooling provided by the treated gas passing through the second side 7b of the heat exchanger 7.

[0019] Each of the additional heat exchangers 12 is connected to a mixing device 13 in turn connected to a supply of a liquid such as methanol and a supply of dry ice (solid carbon dioxide).

[0020] Different positions are possible for the additional heat exchangers 12 in the cryogenic unit 1, for example, the additional heat exchangers 12 can be positioned:

- upstream of the first side 7a of the heat exchanger 7, and/or
- between the first side 7a of the heat exchanger 7 and the gas treatment device 10 (i.e. upstream and/or downstream of the expansion valve 9), and/or
- between the second side 7b of the heat exchanger 7 and the gas treatment device 10.

[0021] In a preferred embodiment, the gas treatment device 10 is a separation device, for separating the gas into its components; for example the separation device is a distillation column.

[0022] Different possibilities for making the methanol and the dry ice available exist.

[0023] Preferably, a reservoir 15 for storing the methanol and a reservoir 16 for storing the dry ice are provided.

[0024] Methanol and dry ice can be supplied into the reservoirs 15, 16 by external sources, e.g. methanol and/or dry ice can be bought on the market and supplied into the reservoirs 15 and/or 16.

[0025] Alternatively or in addition, methanol and dry ice can be produced on site if carbon dioxide is available. This is possible in case the cryogenic unit 1 is used in a power plant, such as an oxyfuel power plant. For example, any carbon capture & storage plant (CCS) and/or carbon capture & utilization plant (CCU) can implement the present invention.

[0026] The attached figures show an oxyfuel power plant having, in addition to the cryogenic unit 1, a boiler 20 supplied with oxygen 21 from the cryogenic unit 1 and fuel 22 (reference 23 indicates nitrogen and other gas from the cryogenic unit 1 that are separated at the distillation column 10 and pass through the heat exchanger 7 via a different path from the path of the oxygen).

[0027] At the boiler 20 combustion of fuel (e.g. coal or oil or in general any carbon containing fuel, either solid, liquid or gaseous) occurs with generation of flue gas that is sent through an air quality control system 25 including e.g. a dust removal unit such as a fabric filter or electrostatic precipitator, a deSO_x unit for sulphur removal, a deNO_x unit for nitrogen removal (if required according to the specific application), a dryer, etc..

[0028] The cleaned flue gas is supplied to a gas processing unit 26 for separating the carbon dioxide from

other gas constituting the flue gas; the carbon dioxide is thus supplied to a pump/compressor 27 for storage (the other gas comprising mainly nitrogen, argon, etc. can be vented from the GPU).

[0029] A part of the carbon dioxide separated from the flue gas can be used to convert carbon dioxide into methanol at a first conversion unit 29 and/or to convert carbon dioxide into dry ice at a second conversion unit 30.

[0030] Processes to convert carbon dioxide into methanol are known in the art; processes to convert gaseous or liquid carbon dioxide into dry ice are known as well.

[0031] The mixing unit 13 can be directly supplied by the first conversion unit 29 and/or second conversion unit 30 or the mixing unit 13 can be directly supplied by the reservoir 15 for the methanol and/or by the reservoir 16 for the dry ice; in addition, it is possible that the first conversion unit 29 is connected to and supplies methanol into the reservoir 15 and/or the second conversion unit 30 is connected to and supplies dry ice into the reservoir 16.

[0032] The operation of the cryogenic unit is apparent from that described and illustrated and is substantially the following. In the following reference to the embodiment of figure 2 is made; in this embodiment the cryogenic unit 1 is part of an air separation unit.

[0033] The gas 3 (e.g. air in case the cryogenic unit is part of an air separation unit ASU or flue gas generated during combustion of a fuel such as coal or oil in case the cryogenic unit is part of a gas processing unit) is compressed at the compressor 2 and is then cooled at the heat exchanger 4, to remove the compression heat; at the compressor a cooling means such as water from an external source or air can be used.

[0034] The gas is thus forwarded to the cleaning system 5 where dust, humidity and carbon dioxide are removed (the treatments occurring in the cleaning system 5 depend on the particular application of the cryogenic unit 1, e.g. in case the cryogenic unit 1 is part of a gas processing unit carbon dioxide is not removed).

[0035] The gas is thus forwarded to the heat exchanger 7 (namely through the first side 7a of the heat exchanger 7). Here the gas is cooled against the treated gas passing through the second side 7b of the heat exchanger 7.

[0036] The cooled gas is thus made to pass through the expansion valve 9 where it is further cooled following expansion.

[0037] As an example, before entering the heat exchanger 7 (i.e. between the cleaning system 5 and heat exchanger 7) the gas has the ambient temperature; after having passed through the heat exchanger 7 (i.e. between the heat exchanger 7 and the expansion valve 9) the gas has a temperature between about -160/-190°C, after having passed through the expansion valve (i.e. between the expansion valve 9 and the gas separation device 10) the gas has a temperature between about -170/-190°C.

[0038] The gas is thus supplied to the gas separation device 10; at the gas separation device 10 the different

gas which constitute the air (nitrogen, oxygen, argon, etc.) are separated. E.g. two or more than two streams can be separated at the gas separation device; in the attached figures all streams separated at the gas separation device are collectively indicated by reference 7b.

[0039] The streams of gas are thus passed through the heat exchanger 12 where the streams are further cooled; the streams can also pass through the heat exchanger 12 without undergoing further cooling or can be bypassed according to the operating conditions and needs.

[0040] The streams are thus passed through the second side 7b of the heat exchanger 7 cooling the gas being treated passing through the first side 7a; the oxygen is then supplied to boiler 20, while the other gas (nitrogen, argon, etc.) is vented via 23 or used in other way.

[0041] The heat exchanger 12 is particularly useful at start up in order to reduce the start-up time. The heat exchanger 12 can also be used during operation in case additional cooling is needed.

[0042] At start up methanol from the reservoir 15 and dry ice from the reservoir 16 are supplied to the mixing unit 13; for example the mixing unit 13 can comprise a tank in which the liquid methanol is contained and one or more feeders to feed the solid dry ice into the liquid methanol. Agitators could also be provided.

[0043] When the solid dry ice is supplied into the methanol (also identified in industry by the abbreviation MeOH), the solid dry ice sublimates, passing from the solid state to the gas state (at least partially); the gaseous carbon dioxide is thus at least partly dissolved in the liquid methanol. This sublimation requires a large amount of heat to occur (because of the high heat of changing of state); the heat for making the sublimation of carbon dioxide to occur is taken from the methanol, which thus becomes colder (e.g. between -60 to -72). Therefore the consequence of mixing dry ice with methanol is the generation of a cold mixture of methanol with carbon dioxide.

[0044] The final temperature depends mainly on the amount of dry ice supplied into the methanol, because of the large heat required for making the sublimation to occur; the exact starting temperature of methanol is less relevant.

[0045] As an example, methanol and dry ice can be mixed in a ration 1:1 by weight.

[0046] It is clear that any liquid can be used instead of methanol, provided that it maintains its liquid state at the operating temperatures reached by the sublimation of dry ice. Use of methanol is anyhow advantageous because it can be produced from the carbon dioxide generated in the power plant and because (even if it contains dissolved carbon dioxide) it can be used as a fuel or supplemental fuel in the power plant itself or in other applications; this way the heat absorbed by the methanol is not lost, but is used in the boiler or other applications.

[0047] The mixture of methanol with carbon dioxide is used in the heat exchanger 12.

[0048] With specific reference to figure 2, when the

stream of gas are cooled in the heat exchanger 12, their temperature is further reduced compared to the temperature at the outlet of the gas treatment device 10; therefore these streams are able at the heat exchanger 7 to cool the gas being treated to a lower temperature than without the additional heat exchanger 12.

[0049] In case the additional heat exchanger has different positions, the cooling occurring there has also the effect of reducing the temperature of the gas being treated directed towards the gas treatment device 10.

[0050] After having passed through the heat exchanger 12, the mixture can be used in different ways. For example the mixture can be used as a fuel in the boiler 20 or as a supplemental fuel in the boiler 20; in this respect the mixture is supplied from the additional heat exchangers to the boiler via lines 31. This is advantageous, because the carbon dioxide contained in the methanol is not vented into the atmosphere, but is treated and collected in the air quality control system 25 and gas processing unit 26.

[0051] The reservoirs 15, 16 can be refilled by methanol and dry ice acquired on the market and/or produced during operation of the power plant.

[0052] As an example, figure 3 shows a gas process unit implementing a cryogenic unit of the invention.

[0053] The gas process unit has a compressor 2 and a gas cleaning system 5 for dust, moisture etc. removal. The gas processing unit further has first and second heat exchangers 7, with a first side 7a for the gas being treated, which in this example is flue gas, and a second side for the treated gas (e.g. nitrogen to be vented, separated carbon dioxide). Downstream of the second heat exchanger 7 a gas separation device in the form of e.g. a distillation column is provided. Also in this example, additional heat exchangers 12 can be provided in different positions.

[0054] Naturally the additional heat exchangers 12 are supplied with a cooling mixture as explained in the previous examples and can be connected to a reservoir 15 and/or reservoir 16 and/or first and/or second conversion units 29, 30.

[0055] The present invention also refers to a method for operating a cryogenic unit 1 for gas treatment.

[0056] The method comprises

- cooling the gas being treated against treated gas by passing the gas being treated through the first side 7a of the heat exchanger 7 and the treated gas through the second side 7b of the heat exchanger 7,
- supplying the cooled gas being treated to the gas treatment device, e.g. for separating the gas being treated into its components,
- mixing a liquid such as methanol and dry ice generating a cooling mixture, this mixture in preferably liquid such that it can be pumped and distributed,
- additionally cooling the gas being treated against the cooling mixture by passing the gas being treated and the cooling mixture through one or more additional

heat exchangers 12.

[0057] Preferably, additionally cooling the gas being treated occurs by:

- additionally cooling the gas being treated upstream of the first side 7a of the heat exchanger 7, and/or
- additionally cooling the gas being treated between the first side 7a of the heat exchanger 7 and the gas treatment device 10, and/or
- additionally cooling the treated gas between the second side 7b of the heat exchanger 7 and the gas treatment device 10.

[0058] In different embodiments, the main flow can pass through the heat exchanger 12 or bypass 17.

[0059] Naturally the features described may be independently provided from one another.

[0060] In practice the materials used and the dimensions can be chosen at will according to requirements and to the state of the art.

REFERENCE NUMBERS

[0061]

- 1 cryogenic unit
- 2 compressor
- 3 gas being treated
- 4 heat exchanger
- 5 cleaning system
- 7 heat exchanger
- 7a first side
- 7b second side
- 9 expansion valve
- 10 gas treatment device
- 12 additional heat exchanger
- 13 mixing device
- 15 reservoir for methanol
- 16 reservoir for dry ice
- 17 bypass
- 20 boiler
- 21 oxygen
- 22 fuel
- 23 other gas
- 25 air quality control system
- 26 gas processing unit
- 27 pump
- 29 first conversion unit
- 30 second conversion unit
- 31 line

Claims

1. A cryogenic unit (1) for gas treatment comprising a heat exchanger (7) having a first side (7a) and a second side (7b),

an expansion valve (9) connected downstream of the first side (7a) of the heat exchanger (7), a gas separation device (10) connected downstream of the expansion valve (9) and upstream of the second side (7b) of the heat exchanger (7), **characterised by** further comprising at least an additional heat exchanger (12), a mixing device (13) connected to the at least an additional heat exchanger (12), a supply of a liquid connected to the mixing device (13), a supply of dry ice connected to the mixing device (13).

2. The unit of claim 1, **characterized in that** the at least an additional heat exchanger (12) is positioned upstream of the first side (7a) of the heat exchanger (7), and/or between the first side (7a) of the heat exchanger (7) and the gas treatment device (10), and/or between the second side (7b) of the heat exchanger (7) and the gas separation device (10).
3. The unit of claim 1, **characterized in that** the gas separation device (10) is a separation device for separating the gas into its components, preferably the separation device is a distillation column.
4. The unit of claim 1, **characterized by** comprising a compressor (2) upstream of the first side (7a) of the heat exchanger (7).
5. The unit of claim 1, **characterized in that** the liquid is methanol.
6. The unit of claim 5, **characterized by** comprising a reservoir (15) for storing the methanol.
7. The unit of claim 1, **characterized by** comprising a reservoir (16) for storing the dry ice.
8. The unit of claim 1, **characterized by** comprising a bypass (17) in parallel to the at least an additional heat exchanger (12).
9. A power plant comprising a boiler (20) generating flue gas and a gas processing unit (26) for separating carbon dioxide from the flue gas, the power plant comprising a cryogenic unit (1) according to any of claims 1 to 8.
10. The power plant of claim 9, **characterized by** further comprising a first conversion unit (29), for converting carbon dioxide into methanol.
11. The system of claim 9, **characterized by** further comprising a second conversion unit (30), for converting carbon dioxide into dry ice.

12. Method for operating a cryogenic unit (1) for gas treatment, wherein the cryogenic unit (1) comprises a heat exchanger (7) having a first side (7a) and a second side (7b),
 an expansion valve (9) connected downstream of the first side (7a) of the heat exchanger (7),
 a gas treatment device (10) connected downstream of the expansion valve (9) and upstream of the second side (7b) of the heat exchanger (7),
 the method comprising
 cooling the gas being treated against treated gas by passing the gas being treated through the first side (7a) of the heat exchanger (7) and the treated gas through the second side (7b) of the heat exchanger (7),
 supplying the cooled gas being treated to the gas treatment device (10),
characterised by
 mixing a liquid and dry ice generating a cooling mixture,
 additionally cooling the gas being treated against the cooling mixture by passing the gas being treated and the cooling mixture through at least an additional heat exchanger (12).
13. The method of claim 12, **characterized in that** additionally cooling the gas being treated occurs by additionally cooling the gas being treated upstream of the first side (7a) of the heat exchanger (7), and/or additionally cooling the gas being treated between the first side (7a) of the heat exchanger (7) and the gas treatment device (10), and/or additionally cooling the treated gas between the second side (7b) of the heat exchanger (7) and the gas treatment device (10).
14. The method of claim 12, **characterized by** separating the gas being treated into its components at the gas treatment device (10).
15. The method of claim 12, **characterized in that** the liquid is methanol.

Fig. 1

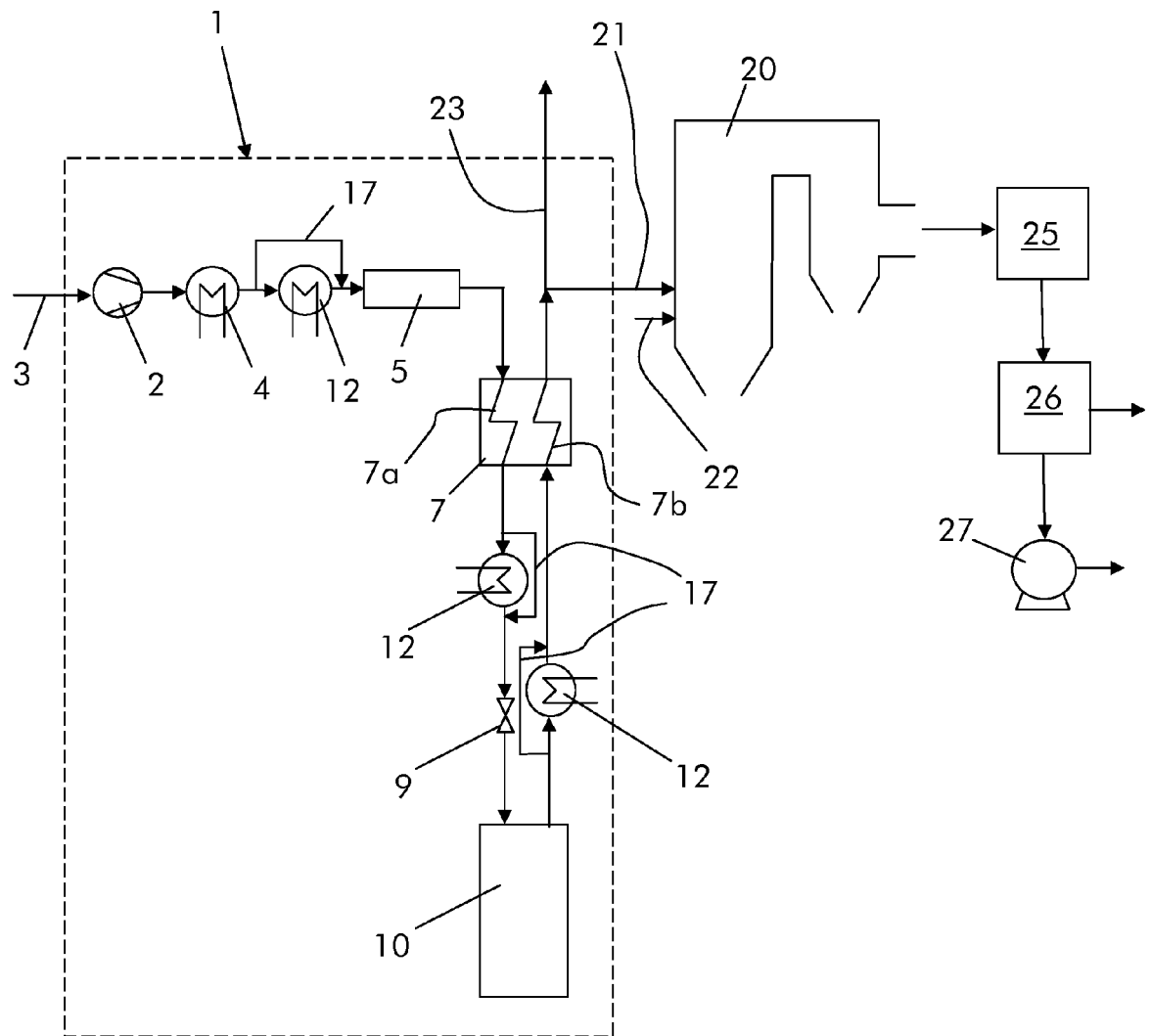


Fig. 2

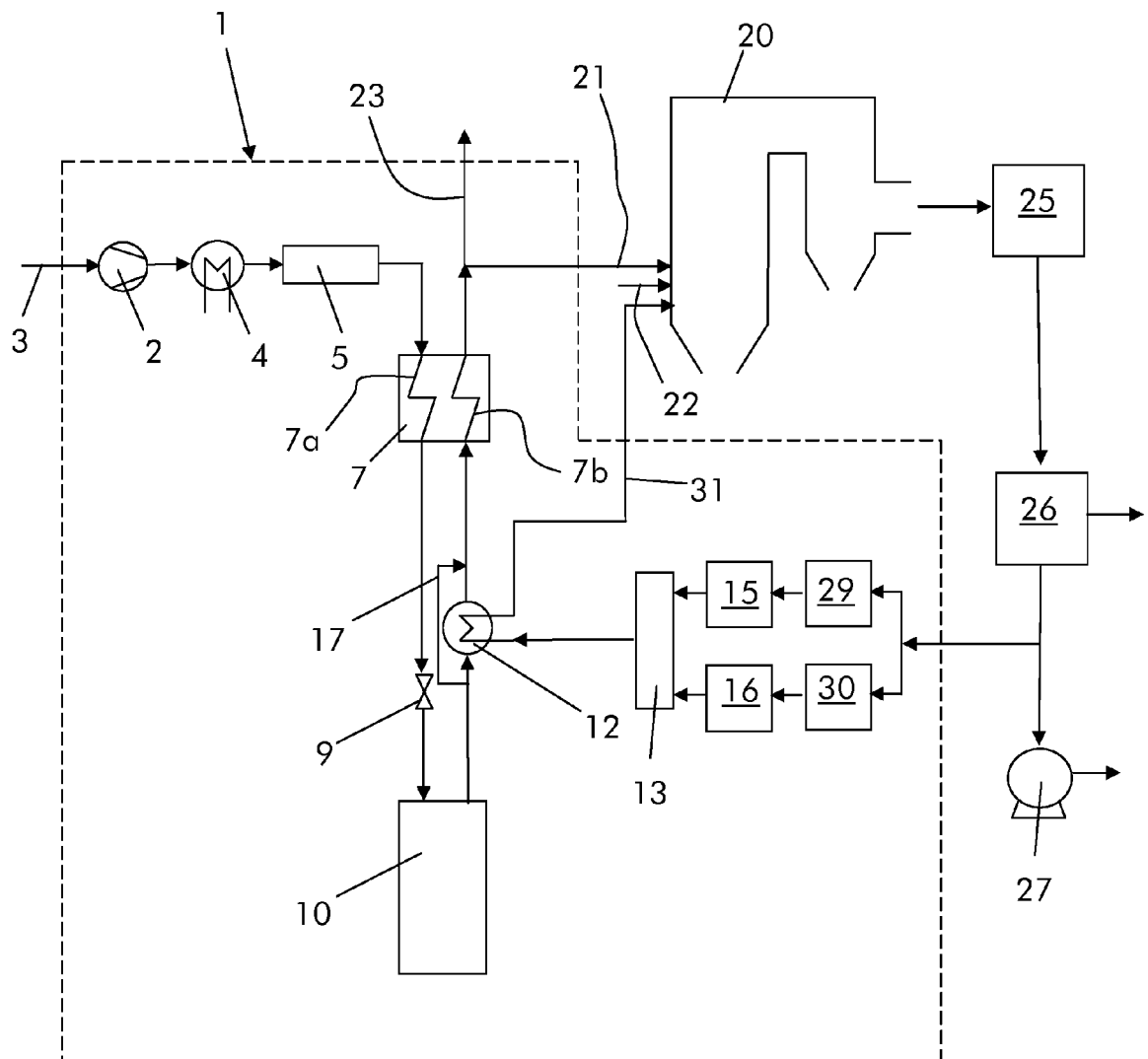
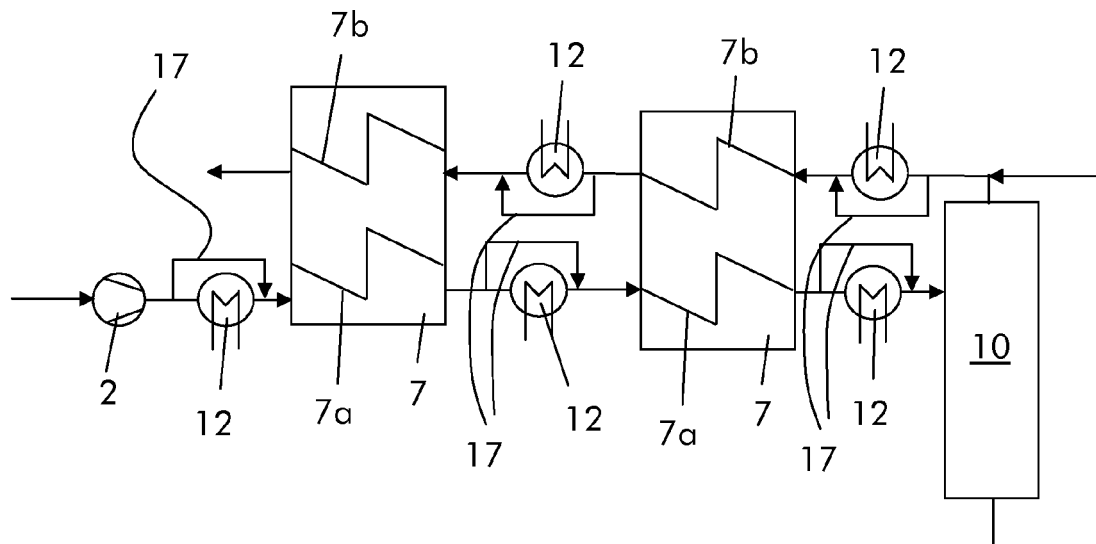


Fig. 3





EUROPEAN SEARCH REPORT

 Application Number
 EP 15 18 5769

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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)
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 June 2016	Examiner Schopfer, Georg
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 03/82 (P04C01)



Application Number

EP 15 18 5769

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☒ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

1, 3-8, 12, 14, 15(completely); 2, 13(partially)

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



LACK OF UNITY OF INVENTION
SHEET B

Application Number

EP 15 18 5769

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1, 3, 4, 8, 12, 14(completely); 2, 13(partially)

Searchable Invention

2. claims: 2, 13(all partially)

The additional heat exchanger is positioned upstream of the first side of the heat exchanger.

3. claims: 5, 6, 15

The liquid is methanol

4. claim: 7

The cryogenic unit contains a reservoir for storing the dry ice.

5. claims: 9-11

Power plant comprising a boiler generating flue gas and a gas processing unit for separating carbon dioxide from the flue gas.

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

EP 15 18 5769

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82