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(54) **Title**: PROCESS AND APPARATUS FOR THE PRODUCTION OF OXYGEN AT HIGH PRESSURE BY CRYOGENIC DISTILLATION

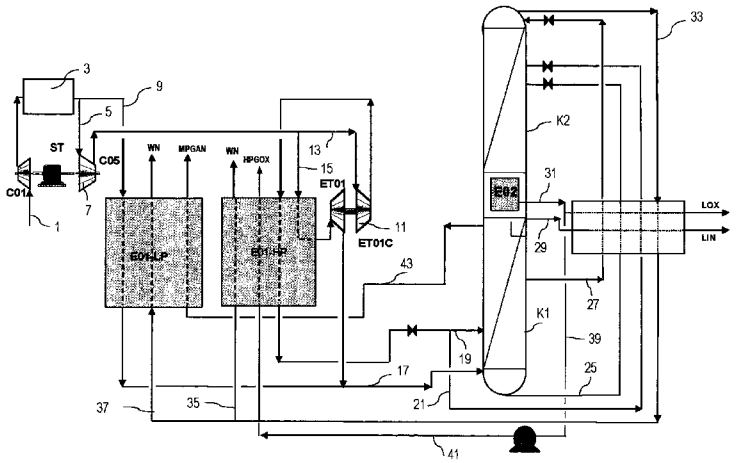

Fig. 1

(57) **Abstract**: In a process for the production of oxygen at a pressure of at least 70 bars abs by cryogenic distillation of air, compressed air (1) is cooled in an exchanger system (E01-LP,E01-HP) and sent to a column system (K1,K2) wherein it is separated to form a liquid (31) containing at least 80% mol. oxygen and a fluid (33) rich in nitrogen and a quantity Q of the said liquid (31) is removed from the column system (K1,K2), pressurized to a vaporization pressure Pv of at least 70 bars abs and vaporized in an exchanger (EOl-HP) of the exchanger system (EOl-LPJiOl-HP) wherein at least one air stream (13,15) is sent to the exchanger (EOl-HP) in which the liquid (31) vaporizes and the highest pressure of any air stream (13,15) sent to the exchanger in which the liquid (31) vaporizes is a pressure P which is less than or equal to Pv and wherein, if any liquid product is produced by the process, the total amount of liquid product or products is less than 20% of Q.

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Process and apparatus for the production of oxygen at high pressure by cryogenic distillation

The present invention relates to a process and an apparatus for the production of oxygen at high pressure by cryogenic distillation.

It is known to produce a high pressure oxygen stream by pressurizing a liquid oxygen stream and vaporizing it under pressure by heat exchange with a stream of air at high pressure. The air pressure is generally 2,3 times higher than the pressure of the oxygen, as mentioned in 89 AIChE Symposium Series 294, "Modern Liquid Pump Oxygen Plants: Equipment and Performance", No. 294 by W.F. Castle, BOC Process Plants, p 14. In WO-A- 2010/088121 a pressure range for the air is defined which is significantly higher than the oxygen vaporisation pressure.

All the pressures mentioned in this document are absolute pressures.

It is also known that a certain number of precautions should be taken in designing and manufacturing brazed aluminium heat exchangers to be used at high pressures.

These include:

- Limitation of the size of the exchanger cores (stacking height and width of the parting sheets)
- Choice of fins adapted to high pressures : herringbone type fins or thick fins with a high fpi are suitable
- Thickness of the parting sheets for the heat exchangers
- Increasing the thickness of the brazing material plating to 200 µm or more
- Possibly asymmetric thickness for the brazing material plating
- Width of side bars and end bars
- Limitation of the header diameters and reinforcement of the regions to which they are fixed

There is a growing need to produce oxygen at pressures of 70 bars or more. The prior art would imply the use of a stream of high pressure air at a pressure of at least 100 bars, to produce oxygen at pressure of 70 bar or more.

The process of this invention can be used to produce oxygen at a pressure at least up to 110 bars without the need of using a stream of air at higher pressure.

The design and manufacture of brazed aluminium heat exchangers for high pressure applications is particularly demanding.

According to the present invention, there is provided a process for the production of oxygen at a pressure of at least 70 bars abs by cryogenic distillation of air in which

i) compressed air is cooled in an exchanger system and sent to a column system wherein it is separated to form a liquid containing at least 80% mol. oxygen and a fluid rich in nitrogen, and

ii) a quantity Q of the said liquid is removed from the column system, pressurized to a vaporization pressure Pv of at least 70 bars abs and vaporized in an exchanger of the exchanger system

wherein at least one air stream is sent to the exchanger in which the liquid vaporizes and the highest pressure of any air stream sent to the exchanger in which the liquid vaporizes is a pressure P which is less than or equal to Pv and wherein, if any liquid product is produced by the process, the total amount of liquid product or products is less than 20% of Q.

According to further objects of the invention:

- less than 40%, or even less than 25%, of the air cooled in the exchanger system is constituted by the air stream at pressure P which is sent to the exchanger in which the liquid vaporizes and which constitutes a first air stream.
- part of the air sent to the exchanger system is at a pressure substantially equal to the pressure of the column of the column system having the highest pressure.
- the ratio P/Pv is less than or equal to 0.9.
- the ratio P/Pv is less than or equal to 0.87.
- the ratio P/Pv is greater than 0.4.
- the exchanger system comprises a first exchanger and a second exchanger and wherein the first exchanger cools an air stream at below 7 bars and above 1 bar against at least one nitrogen stream at a pressure of below 7 bars abs and above 1 bars abs and the liquid vaporizes in the second exchanger in which all the streams, except one or two nitrogen streams from the column system, are at pressures of above 50 bars , even above 60 bars but below 110 bars abs, the air stream at pressure P being cooled in the second exchanger.
- an air stream is sent to the second exchanger, cooled, expanded in a turbine and sent to at least one column of the column system.

- the column system comprises a high pressure column and a low pressure column.
- the air from the turbine is sent to the high pressure column.
- the air stream at pressure P is cooled in the second heat exchanger, expanded in a valve or a liquid turbine and sent to the column system in liquid form.
- the total amount of liquid product or products is less than 10% of Q.

According to the present invention, processes are used in which the ratio between the pressure of the high pressure air and the high pressure oxygen to be vaporised is equal to or less than 1. In this case, it transpires that, surprisingly, the energy penalties are not very great, so long as the oxygen pressure is at least 70 bars abs.

These penalties are more than compensated by the simplification of the air compressors and of the brased aluminium heat exchangers.

The high pressure air can be produced from a booster air compressor fed by air from an adsorbant drying unit.

The high pressure air can be obtained from the outlet of a brake compressor, coupled to one or more cryogenic turboexpanders.

The brake compressor may have an inlet temperature which is around ambient temperature or much colder, as for example a cold compressor.

The heat exchanger used to vaporize the liquid oxygen at a vaporization pressure Pv at or above 70 bars may receive only one other stream which is an air stream at a pressure of less than Pv bars abs.

Otherwise the heat exchanger may not only vaporize liquid oxygen at the pressure Pv but also warm other streams from the column system and/or cool air and/or nitrogen streams at pressures less than Pv.

The process may produce liquid (ie at least one final liquid product which is rich in oxygen, nitrogen or argon). However the process should produce a total quantity of liquid product or products which does not exceed 20% of the liquid rich in oxygen removed from the low pressure column, or preferably which does not exceed 10% of the liquid rich in oxygen removed from the low pressure column or even not exceeding 5% of the liquid rich in oxygen removed from the low pressure column.

The invention will be described in greater details with reference to the figures, Figures 1, 2 and 5 illustrating processes according to the invention and Figures 3 and 4 illustrating heat exchange diagrams for Figures 1 and 2 respectively.

All the processes use a double column, including a high pressure column K1 operating at around 6 bars and a low pressure column K2 operating at around 1.5 bars. The column are thermally coupled via a two stage bath vaporized E02 in the bottom of the low pressure column.

In Figure 1, a stream of air 1 is compressed to between 5 and 6 bars in a compressor C01, purified in a purification system 3 to remove water and carbon dioxide and divided in two. One fraction 5 representing 35% of the air is compressed in booster compressor 7 to a pressure lower than 88 bars, for example 70 bars or even as low as 38 bars and is divided in two. One stream 13 is compressed to 76 bars and sent to high pressure exchanger E01-HP where it is cooled. The cooled stream 13 is divided into streams 19 and 21, one of which is sent to the low pressure column K2 and the other of which is sent to high pressure column K1. The other stream 15 is partially cooled in exchanger E01-HP and expanded in turboexpander ET01, coupled to booster compressor 11, down to the pressure of column K1.

A low pressure air stream is taken from as stream 9 and sent to the low pressure heat exchanger E01-LP, cooled and mixed with the expanded stream 15 before being sent to the high pressure column K1 as stream 17.

High pressure column K1 operates at between 5 and 6 bars abs and low pressure column K2 operates at between 1.3 and 2 bars abs. The columns are thermally linked by a vaporizer E02 which is warmed by high pressure column nitrogen and warms the bottom liquid of the low pressure column K2.

Liquid oxygen 31 is removed from the bottom of the low pressure column and divided in two. One part forms the liquid product LOX and the rest is pressurized by pump P03 up to 88 bars abs. The pressurized oxygen is vaporized in the high pressure heat exchanger E01-HP to form high pressure oxygen HPGOX at 88 bars abs.

Low pressure nitrogen 33 is warmed in subcooler 23 and then divided in two, one part 35 being sent to the high pressure exchanger E01-HP and the rest 37 being sent to the low pressure exchanger E01-LP. The warmed streams are waste nitrogen streams WN. A stream of medium pressure nitrogen 43 is warmed in the low pressure exchanger E01-LP to form stream MPGAN.

In this way, the highest pressure of any air stream sent to the high pressure exchanger is that of stream 13, 76 bar abs and the highest pressure for an oxygen stream being that of oxygen stream 41 at 88 bars abs.

All the streams sent to the low pressure exchanger E01-HP are at pressures lower than 7 bars abs.

In Figure 2, the main compressor C01 and a booster compressor 7 are coupled to a steam turbine. The compressed air is purified in unit 3 and then divided into stream 5 and stream 9. The stream 5 sent to the compressor 7 is divided in two, one part 13 being compressed to 76 bars abs in a compressor C05-2,driven by a steam turbine, and sent to the high pressure heat exchanger E01-HP.

The rest of the air 15 is compressed to a pressure of at most 88 bars, for example 70 bars or even as low as 38 bars, cooled in exchanger E01-HP to an intermediate temperature thereof and entirely expanded in turboexpander ET01 before being mixed with stream 9 downstream of the exchangers.

Stream 13 is cooled in heat exchanger E01-HP, expanded and divided between columns K1 and K2 as streams 19, 21.

The air stream 9 coming from unit 3 is cooled in the low pressure heat exchanger E01-LP to form a stream of cold air.

High pressure column K1 operates at between 5 and 6 bars abs and low pressure column K2 operates at between 1.3 and 2 bars abs.

Liquid oxygen 31 is removed from the bottom of the low pressure column and divided in two. One part forms the liquid product LOX and the rest is pressurized by pump P03 up to 88 bars abs. The pressurized oxygen is vaporized in the high pressure heat exchanger E01-HP.

Low pressure nitrogen 33 is warmed in subcooler 23 and then divided in two, one part 35 being sent to the high pressure exchanger E01-HP and the rest 37 being sent to the low pressure exchanger E01-LP. A stream of medium pressure nitrogen 43 is warmed in the high pressure exchanger E01-HP.

In this way, the highest pressure of any air stream sent to the high pressure exchanger is that of stream 13, 76 bar abs and the highest pressure for an oxygen stream being that of oxygen stream 41 at 88 bars abs.

All the streams 9, 37, 43 sent to the low pressure exchanger E01-HP are at pressures lower than 7 bars abs.

Figure 3 shows the heat exchange diagram for Figure 1 and Figure 4 that of Figure 2.

In Figure 5, a version of Figure 1 is shown in which the air stream at high pressure 13 is cooled in the heat exchanger at 76 bars abs and then expanded in a liquid turbine

51 driving a generator. The liquid formed is divided between columns K1 and K2 in streams 19 and 21.

For all of Figures 1,2 and 5, the flowrate of the oxygen to be vaporized is less than the flowrate of the air at the vaporization pressure, against which the oxygen vaporizes.

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Claims

1. Process for the production of oxygen at a pressure of at least 70 bars abs by cryogenic distillation of air in which

i) compressed air is cooled in an exchanger system (E01-LP, E01-HP) and sent to a column system (K1,K2) wherein it is separated to form a liquid (43) containing at least 80% mol. oxygen and a fluid (33) rich in nitrogen and

ii) a quantity Q of the said liquid is removed from the column system, pressurized to a vaporization pressure Pv of at least 70 bars abs and vaporized in an exchanger (E01-HP) of the exchanger system

wherein at least one air stream (13, 15) is sent to the exchanger in which the liquid vaporizes and the highest pressure of any air stream sent to the exchanger in which the liquid vaporizes is a pressure P which is less than or equal to Pv and wherein, if any liquid product is produced by the process, the total amount of liquid product or products is less than 20% of Q.

2. Process according to Claim 1 wherein less than 40% of the air cooled in the exchanger system (E01-LP, E01-HP) is constituted by the air stream (13) at pressure P which is sent to the exchanger (E01-HP) in which the liquid vaporizes and which constitutes a first air stream.

3. Process according to Claim 2 wherein part (9) of the air sent to the exchanger system (E01-LP, E01-HP) is at a pressure substantially equal to the pressure of the column of the column system having the highest pressure.

4. Process according to any preceding claim wherein the ratio P/Pv is less than or equal to 0.9.

5. Process according to Claim 4 wherein the ratio P/Pv is less than or equal to 0.87.

6. Process according to any preceding claim wherein the ratio P/Pv is greater than 0.4.

7. Process according to any preceding claim wherein the exchanger system (E01-LP, E01-HP) comprises a first exchanger (E01-LP) and a second exchanger (E01-HP) and wherein the first exchanger cools an air stream at below 7 bars and above 1 bar against at least one nitrogen stream at a pressure of below 7 bars abs and above 1 bars abs and the liquid vaporizes in the second exchanger in which all the streams, except one or two nitrogen streams from the column system, are at pressures of above 50 bars, even above 60 bars but below 110 bars abs, the air stream at pressure P being cooled in the second exchanger.

8. Process according to Claim 7 wherein an air stream is sent to the second exchanger (E01-HP), cooled, expanded in a turbine (ET01) and sent to at least one column of the column system.

9. Process according to Claim 7 or 8 wherein the column system comprises a high pressure column (K1) and a low pressure column (K2).

10. Process according to Claim 8 and 9 wherein the air from the turbine (ET01) is sent to the high pressure column (K1).

11. Process according to Claim 7,8,9 or 10 wherein the air stream at pressure P is cooled in the second heat exchanger (E01-HP), expanded in a valve or a liquid turbine and sent to the column system (K1, K2) in liquid form.

12. Process according to any preceding claim wherein the total amount of liquid product or products is less than 10% of Q.

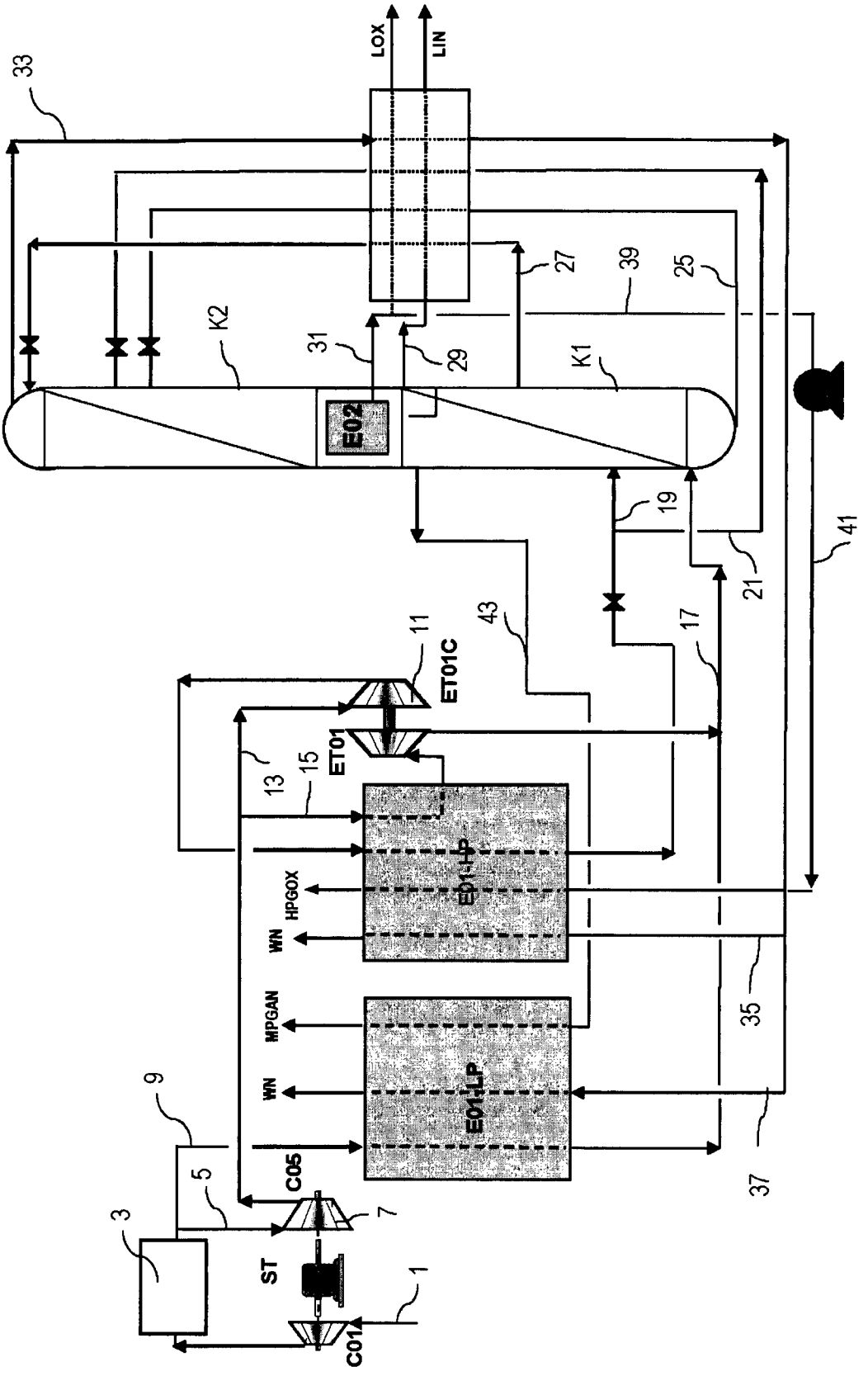
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Fig. 1

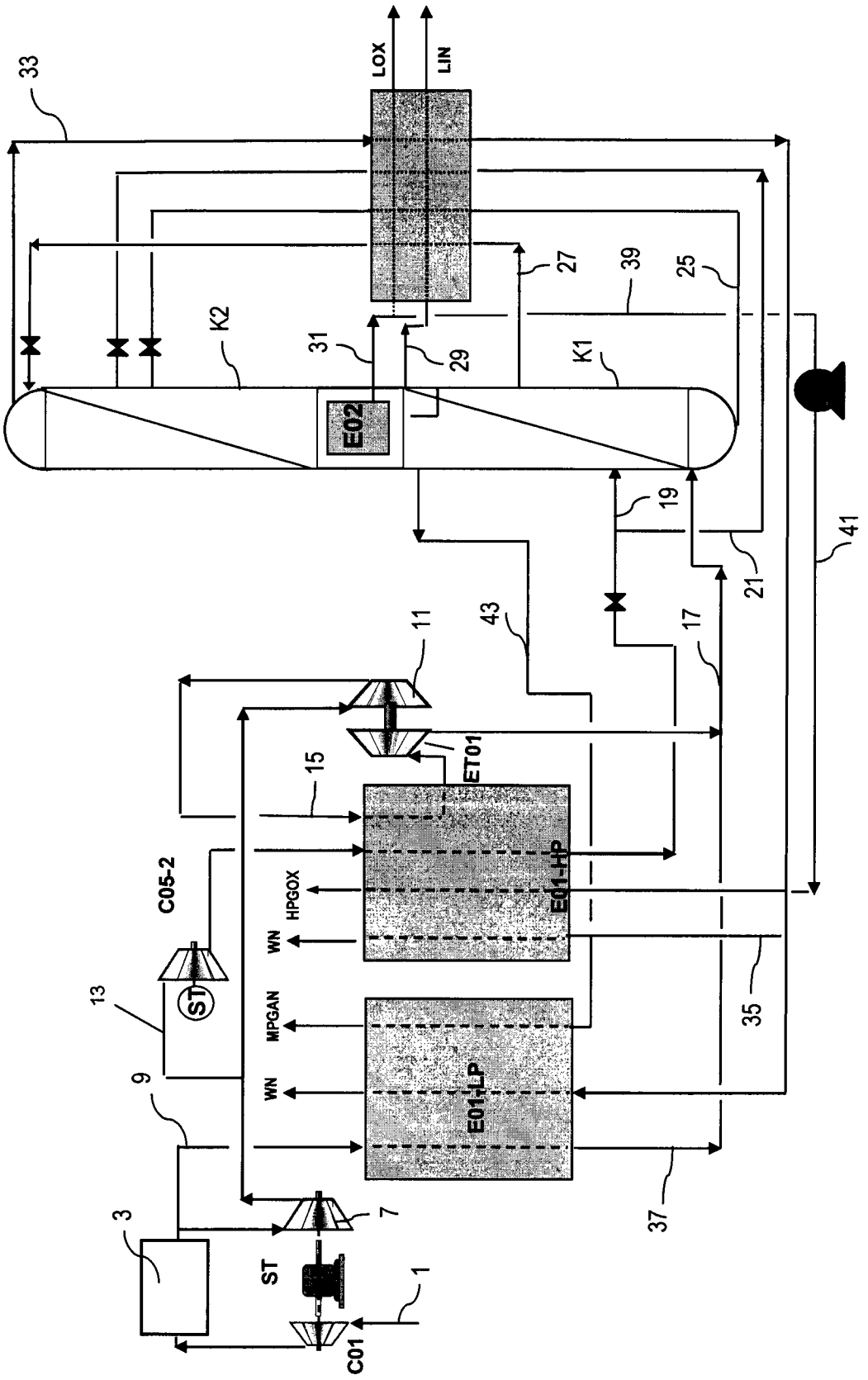
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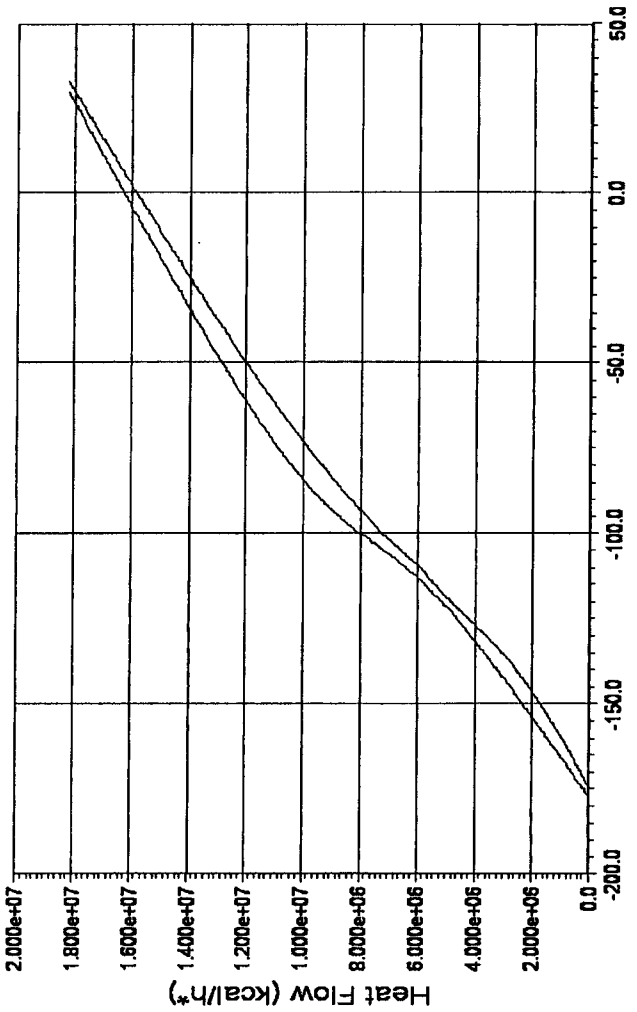
Fig 2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1.800e+07
1.600e+07
1.400e+07
1.200e+07
1.000e+07
8.000e+06
6.000e+06
4.000e+06
2.000e+06
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Temperature (°C)
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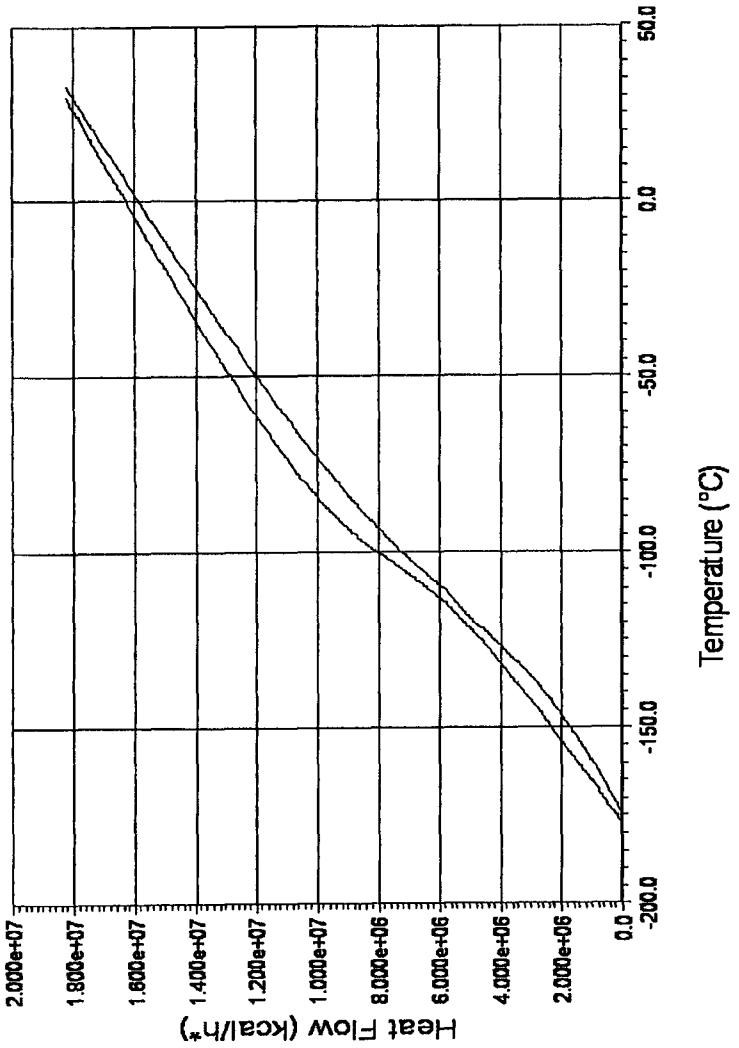
Fig.3


Heat Flow (kcal/h*)
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1.600e+07
1.400e+07
1.200e+07
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8.000e+06
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4.000e+06
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Temperature (°C)

Fig 4

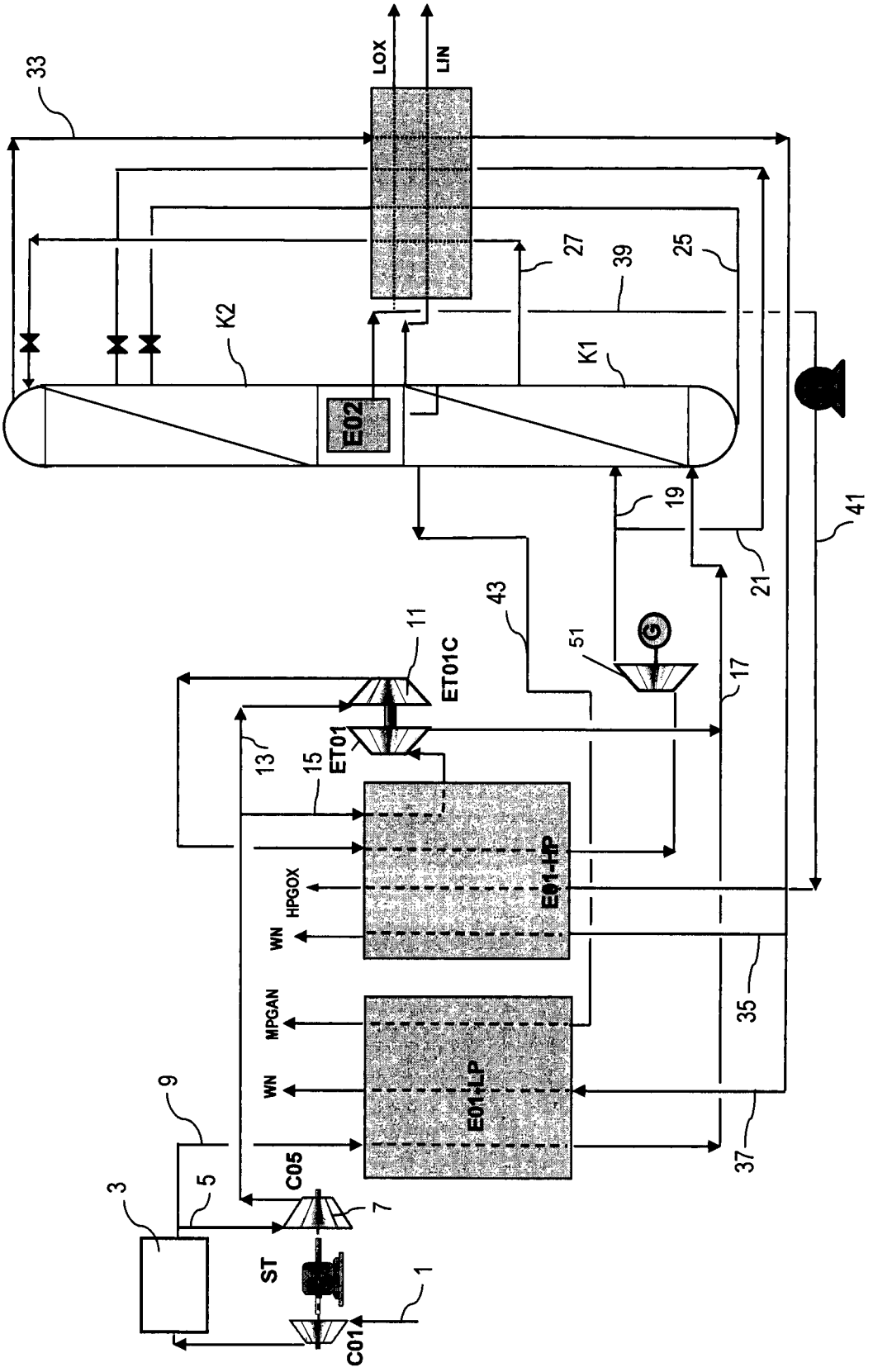
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Fig 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/074027

A. CLASSIFICATION OF SUBJECT MATTER

F25J3/04 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: F25J 3/+

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)

CNABS, EPODOC, WPI: pressure, high, vaporiz+, oxygen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN1071001A (GEORGE CLAUDE TECHNOLOGY RES A) 14 Apr. 1993(14.04.1993) see line 17, page 5 - the last line of page 7 of the description, fig. 1	1-12
A	RU2387934C2 (AIR LIQUIDE SA) 27 Apr. 2010(27.04.2010) see the whole document	1-12
A	FR2831249A1(AIR LIQUIDE) 25 Apr. 2003(25.04.2003) see the whole document	1-12
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A	EP1132700A1(AIR LIQUIDE) 12 Sep.2001(12.09.2001) see the whole document	1-12
A	FR2831250A1(AIR LIQUIDE) 25 Apr. 2003(25.04.2003) see the whole document	1-12

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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

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

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

"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
09 Feb.2012(09.02.2012)	**23 Feb. 2012 (23.02.2012)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer XIA,Lei Telephone No. (86-10)62084716

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/074027

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