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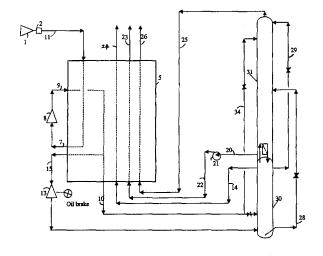
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# (54) Process and apparatus for the separation of air by cryogenic distillation

A process for separating air by cryogenic distillation in a column system comprising a high pressure column and a low pressure column comprises compressing all the feed air in a first compressor (1) to a first outlet pressure, sending a first part of the air at the first outlet pressure to a second compressor (3) and compressing the air to a second outlet pressure, cooling at least part of the air at the second outlet pressure in a heat exchanger (5) liquefying at least part of the air at the second outlet pressure and sending the liquefied air to at least one column of the column system wherein at least 50% of the liquefied air sent to the column system has been compressed in the second compressor, cooling a second part of the air (12) at the first outlet pressure in the heat exchanger and expanding at least part of the second part of the air in an expander (13) from the first outlet pressure to the pressure of a column (30,31) of column system and sending the expanded air to that column, at least partially vaporizing an auxiliary fluid (6), eventually further warming said auxiliary fluid in the heat exchanger, sending at least part of this auxiliary fluid to a third compressor (8) to a third outlet pressure, introducing at least part (9) of said auxiliary fluid at said third outlet pressure in the heat exchanger, cooling said auxiliary fluid and at least partially liquefying said auxiliary fluid, removing said auxiliary stream (10) from the heat exchanger and expanding (16) it to a fourth pressure level before reintroducing it in the heat exchanger where it will be partially vaporized as above-mentioned, removing liquid (20) from a column (31) of the column system and vaporizing the liquid by heat exchange in the heat exchanger.



Prior art

FIG. 1

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**[0001]** The present invention relates to a process and apparatus for the separation of air by cryogenic distillation. It relates in particular to processes and apparatus for producing oxygen and/or nitrogen at elevated pressure.

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[0002] Gaseous oxygen produced by air separation plants are usually at elevated pressure about 20 to 50 bar. The basic distillation scheme is usually a double column process producing oxygen at the bottom of the low-pressure column operated at 1.4 to 4 bar. The oxygen must be compressed to higher pressure either by oxygen compressor or by the liquid pumping process. Because of the safety issues associated with the oxygen compressors, most recent oxygen plants are based on the liquid pumping process. In order to vaporize liquid oxygen at elevated pressure there is a need for an additional motor-driven booster compressor to raise a portion of the feed air or nitrogen to higher pressure in the range of 40-80 bars. In essence, the booster replaces the oxygen compressor.

**[0003]** In the effort to reduce the complexity of an oxygen plant, it is desirable to reduce the number of motor-driven compressors. Significant cost reduction can be achieved if the booster can be eliminated without much affecting the plant performance in terms of power consumption. Furthermore, the air purification unit conceived for a traditional oxygen plant would operate at about 5-7 bar which is essentially the pressure of the high-pressure column, and it is also desirable to raise this pressure to a higher level in order to render the equipment more compact and less costly.

[0004] A cold compression process as described in US-A-5,475,980 provides a technique to drive the oxygen plant with a single air compressor. In this process, air to be distilled is chilled in the main exchanger then further compressed by a booster compressor driven by an expander exhausting into the high-pressure column of a double column process. By doing so, the discharge pressure of the air compressor is in the range of 15 bar which is also quite advantageous for the purification unit. One inconvenience of this approach is the increase of the size of the main exchanger due to additional flow recycling which is typical for the cold compression plant. One can reduce the size of the exchanger by opening up the temperature approaches of the exchanger. However, this would lead to inefficient power usage and higher discharge pressure of the compressor, therefore increasing its cost. An illustration of this prior art is presented in Figure 1, in which an oil brake is added to the system to dissipate the power required for the refrigeration. In larger plants, a compressor and/or a generator can replace the oil brake.

**[0005]** In Figure 1 all the feed air is compressed in compressor 1, purified in purification unit 2 and sent as stream 11 to the warm end of the heat exchanger 5. All the feed air is cooled to an intermediate temperature, removed

from the heat exchanger as stream 7 and compressed in cold compressor 8. The compressed stream 9 is sent back to the heat exchanger at a higher intermediate temperature, cooled to a temperature lower than the inlet temperature of the cold compressor 8 and divided in two. Stream 15 is sent to the Claude expander 13 which is braked by the compressor 8 and an oil brake. The rest of the air 10 is liquefied in the heat exchanger and divided into two parts, one part being sent to the high-pressure column 30 and the rest 34 being sent to the low-pressure column 31.

[0006] An oxygen enriched liquid stream 28 is expanded and sent from the high-pressure column to the low-pressure column. A nitrogen enriched liquid stream 29 is expanded and sent from the high-pressure column to the low-pressure column. High-pressure gaseous nitrogen 14 is removed from the top of the high-pressure column and warmed in the heat exchanger to form a product stream 24. Liquid oxygen 20 is removed from the bottom of the low pressure column 31, pressurized by a pump 21 and sent as stream 22 to the heat exchanger 5 where it vaporizes by heat exchange with the pressurized air 10 to form gaseous pressurized oxygen 23. A top nitrogen enriched gaseous stream 25 is removed from the low-pressure column 31, warmed in the heat exchanger 5 and then forms stream 26.

**[0007]** Some different versions of the cold compression process were also described in prior art as in US-A-5379598, US-A-5596885, US-A-5901576 and US-A-6626008.

**[0008]** In US-A-5379598 a fraction of feed air is further compressed by a booster compressor followed by a cold compressor to yield a pressurized stream needed for the vaporization of oxygen. This approach still has at least two compressors and the purification unit still operates at low pressure.

**[0009]** In US-A-5596885, a fraction of the feed air is further compressed in a warm booster whilst at least part of the air is further compressed in a cold booster. Air from both boosters is liquefied and part of the cold compressed air is expanded in a Claude expander.

**[0010]** US-A-5901576 describes several arrangements of cold compression schemes utilizing the expansion of vaporized rich liquid of the bottom of the high-pressure column, or the expansion of high-pressure nitrogen to drive the cold compressor. In some cases, motor driven cold compressors were also used. These processes also operate with feed air at about the high-pressure column's pressure and in most cases a booster compressor is also needed.

[0011] US-A-6,626,008 describes a heat pump cycle utilizing a cold compressor to improve the distillation process for the production of low purity oxygen for a double vaporizer oxygen process. Low air pressure and a booster compressor are also typical for this kind of process.

**[0012]** Therefore it is a purpose of this invention to resolve the inconveniences of the traditional process by

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providing a solution to simplify the compression train and to reduce the size of the purification unit. This can moreover be achieved with good power consumption. The overall product cost of an oxygen plant can therefore be reduced. The main improvement in power consumption is due to the reduction in the cold compressor flow by using essentially latent heat instead of specific heat.

[0013] All percentages listed are molar percentages.
[0014] According to the present invention, there is provided a process for separating air by cryogenic distillation in a column system comprising a high pressure column and a low pressure column comprising the steps of:

- i) compressing all the feed air in a first compressor to a first outlet pressure
- ii) sending a first part of the air at the first outlet pressure to a second compressor and compressing the air to a second outlet pressure
- iii) cooling at least part of the air at the second outlet pressure in a heat exchanger to form cooled compressed air at the second outlet pressure, liquefying at least part of the air at the second outlet pressure and sending the liquefied air to at least one column of the column system
- iv) cooling a second part of the air at the first outlet pressure in the heat exchanger and expanding at least part of the second part of the air in an expander from the first outlet pressure to the pressure of a column of column system and sending the expanded air to that column
- v) removing liquid from a column of the column system, pressurizing the liquid and vaporizing the liquid by heat exchange in the heat exchanger
- vi) at least partially vaporizing an auxiliary fluid, eventually further warming said auxiliary fluid in the heat exchanger, sending at least part of this auxiliary fluid to a third compressor to be compressed to a third outlet pressure, introducing at least part of said auxiliary fluid at said third outlet pressure in the heat exchanger, cooling said auxiliary fluid and at least partially liquefying said auxiliary fluid, removing said auxiliary stream from the heat exchanger and expanding it to a fourth pressure level before reintroducing it in the heat exchanger where it will be partially vaporized as above-mentioned.

**[0015]** According to optional features of the invention:

- additional air is liquefied in the heat exchanger at the first pressure.
- the third compressor compresses an auxiliary fluid containing at least one of the following gases: He, H<sub>2</sub>, Ne, N<sub>2</sub>, CO, Ar, O<sub>2</sub>, CH<sub>4</sub>, Kr, NO, Xe, CF<sub>4</sub>, HCF<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, N<sub>2</sub>O, CO<sub>2</sub>.
- the third compressor compresses an auxiliary fluid whose principal component comprises at least one of: Ar, O<sub>2</sub>, CH<sub>4</sub> and Kr.

**[0016]** According to another aspect of the invention, there is provided an apparatus for the separation of air by cryogenic distillation comprising:

- a) a column system
- b) first, second and third compressors
- c) an expander
- d) a conduit for sending air to the first compressor to form compressed air at a first outlet pressure
- e) a conduit for sending a first part of the air at the first outlet pressure to the second compressor to form air at a second outlet pressure
- f) a heat exchanger, a conduit for sending at least part of the air at the second outlet pressure to the heat exchanger to form cooled compressed air at the second outlet pressure,
- g) a conduit for removing liquefied air at the second outlet pressure from the heat exchanger and for sending the liquefied air to at least one column of the column system
- h) a conduit for removing a second part of the air at the first outlet pressure from the heat exchanger and for sending at least part of the second part of the air to the expander
- i) a conduit for sending air expanded in the expander to at least one column of column system
- j) a conduit for removing liquid from a column of the column system, means for pressurizing at least part of the liquid to form pressurized liquid and a conduit for sending at least part of the pressurized liquid to the heat exchanger and
- k) a refrigeration cycle comprising the third compressor and a second expander (16), a conduit for sending an auxiliary fluid from the third compressor to the heat exchanger, a conduit for sending the auxiliary fluid from the heat exchanger to the second expander, a conduit for sending the auxiliary fluid from the second expander to the heat exchanger and a conduit for sending the auxiliary fluid from the heat exchanger to the third compressor.

**[0017]** According to further optional aspects of the invention, the apparatus may include a further expander and means for sending nitrogen from a column of the column system or air to the further expander.

**[0018]** In this case, one of the second and third compressors may be coupled to the expander and the other of the second and third compressors may be coupled to the further expander.

50 **[0019]** At least one of the second and third compressors is coupled to the air expander.

**[0020]** Preferably the conduit for sending a first part of the air at the first outlet pressure to the second compressor is connected to an intermediate point of the heat exchanger.

[0021] Preferably the second and third compressors are connected in series.

[0022] The expander may be chosen from the group

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including an air expander whose outlet is connected to the high pressure column, an air expander whose outlet is connected to the low pressure column, a high pressure nitrogen expander and a low pressure nitrogen expander.

[0023] The apparatus may include a further expander chosen from the group including an air expander whose outlet is connected to the high pressure column, an air expander whose outlet is connected to the low pressure column, a high pressure nitrogen expander and a low pressure nitrogen expander.

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**[0024]** Preferably the further expander is coupled to one of the second and third expanders.

**[0025]** The invention will now be described in greater detail with reference to Figures 2, 3, 5 and 6 which are process flow diagrams representing cryogenic air separation processes according to the invention, Figure 4 which is a heat exchange diagram and to Figure 7 which shows a coupling system for compressors and expanders in a process according to the invention.

**[0026]** In the embodiment of Figure 2, atmospheric air is compressed by the air compressor 1 and purified in the purification unit 2 to yield an air stream (stream 11) free of impurities such as moisture and carbon dioxide that can freeze in the cryogenic equipment. A first portion of this air is compressed in a booster brake compressor 3 to raise its pressure further. This pressurized first portion (stream 4) is then cooled in the main exchanger 5 to condense to form a liquefied air stream (stream 27), which is fed to at least one of the distillation columns, following expansion in a valve. The air may liquefy within or downstream the main exchanger depending on the pressure used. An auxiliary fluid mixture 6 of krypton (90%) and oxygen (10%) is introduced in heat exchanger 5 when it is vaporized and slightly warmed after vaporization to yield a cold auxiliary gaseous stream at an intermediate temperature T1. At least a portion of this cold auxiliary stream (stream 7) is sent to a cold brake compressor 8 at temperature T1 to be compressed to raise its pressure (stream 9). Stream 9 is then sent back to the exchanger at temperature T2 which is greater than T1 and cooled in exchanger 5 to condense to form a liquefied auxiliary stream (stream 10), which is expanded in a valve 16 to form stream 6. A phase separator could be added if stream 6 is a two-phase fluid, the liquid phase being introduced in heat exchanger 5 and the vapor phase mixed with stream 7. The second portion of stream 11 (stream 12) is cooled in exchanger 5 to yield stream 15, which is sent to the expander 13 at an inlet temperature of T3, for expansion into the high pressure column. It is preferable that the power generated by expander 13 be used to drive the booster brake compressor 3. The rest of stream 12 is liquefied as stream 33 and sent to the high pressure column 30. Nitrogen rich gas 14 can be extracted from the high pressure column 30, warmed in exchanger 5 to form stream 17, which is then expanded in expander 18 having an inlet temperature T4. The power of expander 18 can be preferably used to drive the cold booster brake compressor 8. The exhaust of expander 18 (stream 19) then returns to the cold end of exchanger 5 to be re-heated to close to ambient temperature forming stream 24. Pump 21 boosts the pressure of liquid oxygen product 20 extracted at the bottom of the low pressure column 31 to the desired pressure then sends pressurized oxygen stream 22 to exchanger 5 for vaporization and heating to yield the oxygen product 23. The double column system is a traditional type of two-column process as described in numerous patents or papers on air separation technology having a high pressure column 30 and a low pressure column 31, thermally linked by a reboiler-condenser at the bottom of the low pressure column. An argon column (not shown) can be used with the double column system to provide a concentrated argon stream.

**[0027]** The above temperatures T1, T2, T3 and T4 are provided as the preferred arrangement. Above, going from the hottest temperature to the coldest the temperatures are T2, T5, T1 and T3. Depending upon the pressure of the vaporized oxygen and the pressure of the column system the order of these temperatures can be modified to optimize the performance of the process.

[0028] It is useful to note the booster brake compressors 3 is a single stage compressor and is usually provided as part of the expander-booster package and therefore its construction is much simpler and its cost structure much lower than the stand-alone or motor-driven booster compressor. However if necessary, compressor 3 may be a stand-alone or motor-driven booster compressor. Compressor 8 could be either a stand-alone or motor driven booster compressor with one to four stages depending upon the pressure of stream 4 and stream 23. It could be driven directly by expander 18 (alternately expander 13) at the same speed or through a gear to optimize the performances of the booster and expander. [0029] The range of the process variables of the embodiment of Figure 2 is as follows:

Stream 11 pressure: about 9 to 17 bar a
Stream 4 pressure: about 16 to 50 bar a
Stream 9 pressure: about 5 to 20 bar a in case of a
mixture rich in krypton

T1: about -110°C to -165°C

The flow compressed by the booster brake compressor 8 can be reduced by optionally extracting some of stream 12 as liquefied air flow 33. As such, less power is required to drive the booster brake compressor 8 and some power savings can be achieved. The amount of air liquefied at the first pressure should not be more than 50% of the liquefied air sent to the column system, preferably not more than 40%, more preferably not more than 35 %.

[0030] It is common practice in air separation technology to substitute the nitrogen expander with an air expander. The embodiment of Figure 3 describes such an arrangement: after the first compressor, the portion 12 of stream 11 is cooled in exchanger 5 and part of this

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stream is extracted to yield stream 50, which is sent to expander 52 for expansion into the low pressure column 31. The power of expander 52 is preferably used to drive the cold compressor 8. It is useful to note that one can also opt to divide stream 12 before exchanger 5 and send the corresponding air stream to a separate passage in exchanger 5 then cool and expand it in expander 52 into the column. Figure 4 shows the exchange diagram corresponding to the process of Figure 3.

**[0031]** The above technique can be modified slightly as described in Figure 5: a portion 53 of the air at the exhaust stream 54 of expander 13 can be warmed in the exchanger 5 then send to the expander 52 for expansion into the low pressure column. In situations where there is some condensation in stream 54, one can extract the gas feeding the expander 52 by adding a vapor-liquid separator or even better, use the sump of the high pressure column as a separator, in this case, the gas feeding the expander is extracted at the sump of the high pressure column.

[0032] In many situations where there is a need for a significant amount of nitrogen rich gas product at elevated pressure, it is no longer economical to utilize the nitrogen rich gas expander 18. Instead as shown in Figure 6 the nitrogen rich gas 14 can be extracted and produced directly off the high pressure column 30 to yield the nitrogen product 41. In those situations one can opt to raise the pressure of compressor 1 to increase the power output of the expander 13 to cover the lack of refrigeration caused by the elimination of the nitrogen expander. To further simplify the expander and booster brake compressors arrangement, the tandem expander and booster brakes can be mechanically integrated into a single train: the power of the expander 13 drives the two compressor brakes 3 (single stage) and 8 (double stage). In addition, a motor and/or generator 60 can extract or add mechanical power to the system depending on the performance and production expected from the plant at a certain time. Depending upon the flows and pressures of the expander and booster brake compressors a speed changer (gear) can be used to optimize the system performance. An illustration of the arrangement with gear is presented in Figure 7. A further expander 18, 52 could also be added to such a system.

**[0033]** The process may be modified to vaporize pumped liquid nitrogen as an additional stream or as a stream replacing the pumped oxygen stream.

**[0034]** The illustrated processes show double column systems but it will be readily understood that the invention applies to triple column systems.

**[0035]** In the case where the double or triple column systems operate at elevated pressures, some of the low pressure nitrogen may be expanded in an expander 18.

#### **Claims**

1. Process for separating air by cryogenic distillation in

a column system comprising a high pressure column and a low pressure column comprising the steps of:

- i) compressing all the feed air in a first compressor (1) to a first outlet pressure
- ii) sending a first part (4) of the air at the first outlet pressure to a second compressor (3) and compressing the air to a second outlet pressure iii) cooling at least part of the air at the second outlet pressure in a heat exchanger (5)
- iv) cooling a second part (12) of the air at the first outlet pressure in the heat exchanger and expanding at least part of the second part of the air in an expander (13) from the first outlet pressure to the pressure of a column (30) of column system and sending the expanded air to that column
- v) removing liquid (20) from a column (31) of the column system, pressurizing the liquid and vaporizing the liquid by heat exchange in the heat exchanger
- vi) at least partially vaporizing an auxiliary fluid in the heat exchanger, eventually further warming said auxiliary fluid in the heat exchanger, sending at least part of this auxiliary fluid to a third compressor (8) to be compressed to a third outlet pressure, introducing at least part of said auxiliary fluid (9) at said third outlet pressure in the heat exchanger, cooling said auxiliary fluid and at least partially liquefying said auxiliary fluid, removing said auxiliary stream from the heat exchanger and expanding it to a fourth pressure level before reintroducing it (6) in the heat exchanger for the afore mentioned at least partial vaporization step.
- 2. The process of Claim 1 wherein at least part of the first part of the air is cooled upstream of the second compressor (3).
- 3. The process of Claim 2 wherein at least part of the first part of the air is cooled upstream of the second compressor (3) in the heat exchanger (5).
- 45 4. The process of Claim 2 wherein at least part of the first part of the air is cooled upstream of the second compressor in the heat exchanger using a refrigeration unit.
- 50 **5.** The process of Claim 1 to 4 wherein additional air (27, 33) is liquefied in the heat exchanger at at least one of the first and second pressures.
  - 6. The process of Claim 1 to 5 wherein the third compressor compresses an auxiliary fluid chosen from the group comprising containing at least one of the following gases: He, H<sub>2</sub>, Ne, N<sub>2</sub>, CO, Ar, O<sub>2</sub>, CH<sub>4</sub>, Kr, NO, Xe, CF<sub>4</sub>, HCF<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>,

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N<sub>2</sub>O, CO<sub>2</sub>.

The process of Claim 6 wherein a principal component of the auxiliary fluid is at least one of: Ar, O<sub>2</sub>, CH<sub>4</sub> and Kr.

8. Apparatus for the separation of air by cryogenic dis-

a) a column system (30, 31)

b) first, second and third compressors (1, 3, 8)

c) a first expander (13)

tillation comprising:

d) a conduit for sending air to the first compressor to form compressed air at a first outlet pressure

e) a conduit for sending a first part of the air at the first outlet pressure to the second compressor to form air at a second outlet pressure

f) a heat exchanger (5), a conduit for sending at least part of the air at the second outlet pressure to the heat exchanger to form cooled compressed air at the second outlet pressure,

g) a conduit for removing liquefied air at the second outlet pressure from the heat exchanger and for sending the liquefied air to at least one column of the column system

h) a conduit for removing a second part of the air at the first outlet pressure from the heat exchanger and for sending at least part of the second part of the air to the expander conduit for sending air expanded in the expander to at least one column of column system

i) a conduit for removing liquid from a column of the column system, means for pressurizing at least part of the liquid to form pressurized liquid and a conduit for sending at least part of the pressurized liquid to the heat exchanger and j) a refrigeration cycle comprising the third compressor and a second expander (16), a conduit for sending an auxiliary fluid from the third compressor to the heat exchanger, a conduit for sending the auxiliary fluid from the heat exchanger to the second expander, a conduit for sending the auxiliary fluid from the second expander to the heat exchanger and a conduit for sending the auxiliary fluid from the heat exchanger to the third compressor.

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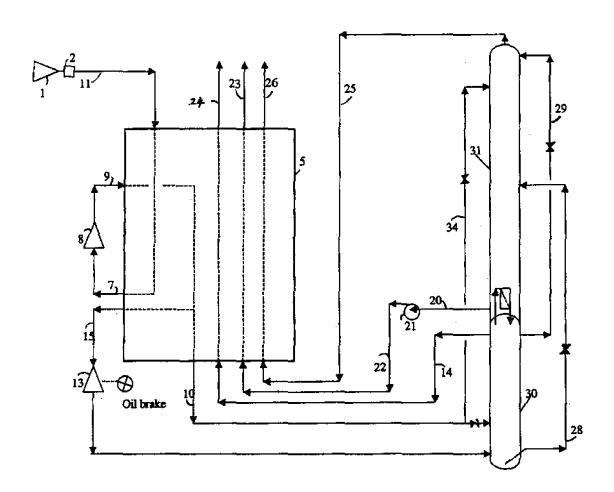
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Prior art

FIG. 1

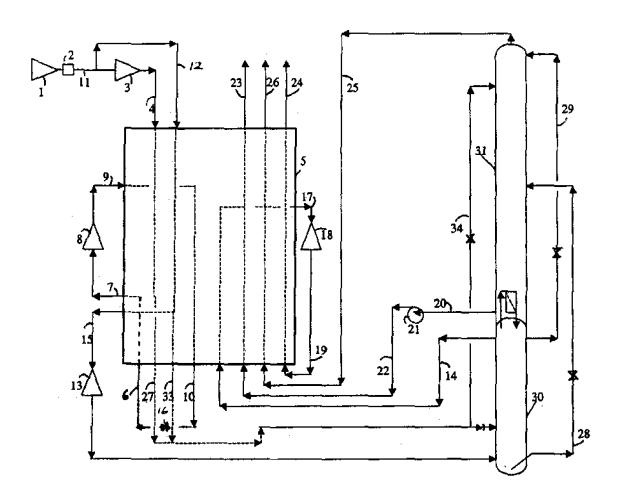


FIG. 2

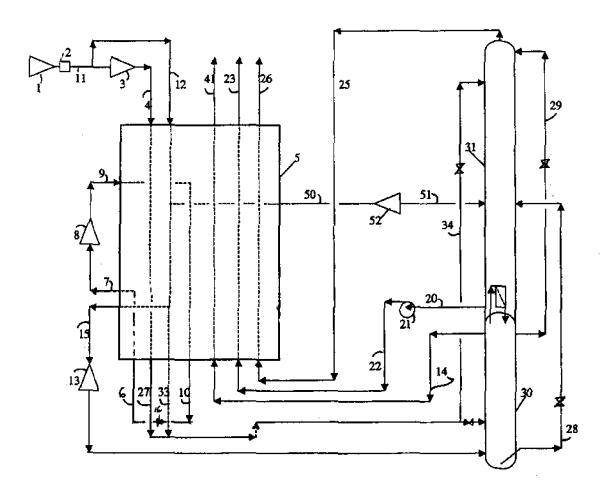
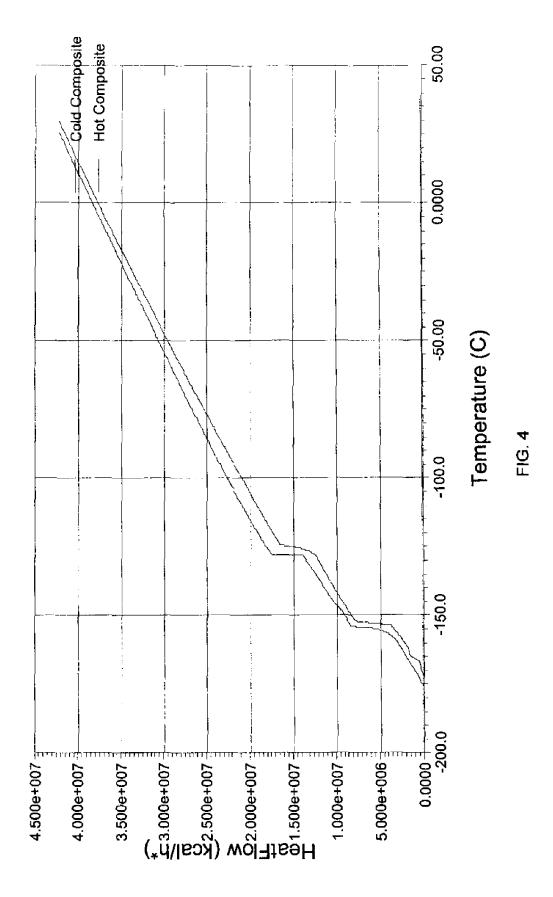


FIG. 3



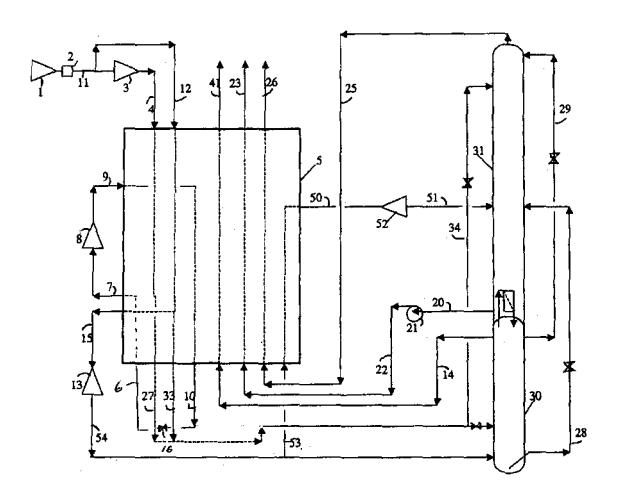


FIG. 5

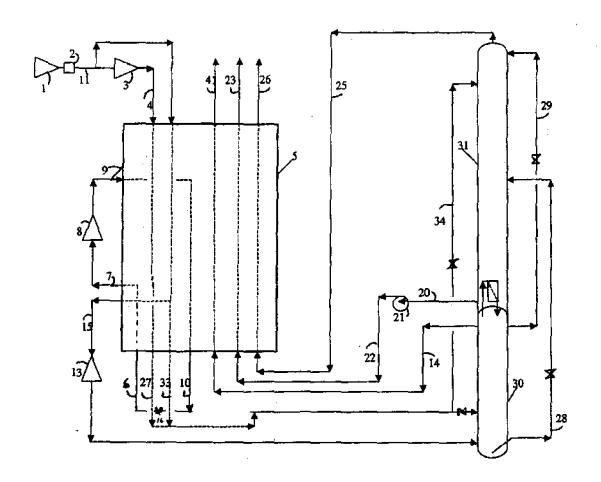


FIG. 6

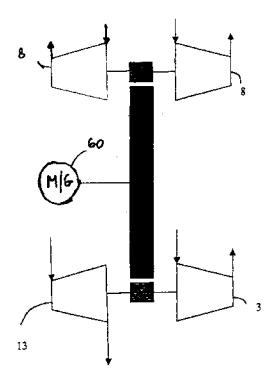


FIG. 7



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Application Number EP 05 10 8826

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

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### REFERENCES CITED IN THE DESCRIPTION

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