(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 746 374 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.01.2007 Bulletin 2007/04

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

(21) Application number: **06117128.6**

(22) Date of filing: **13.07.2006**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **21.07.2005 US 681749 P**

(71) Applicant: **L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE**
75007 Paris (FR)

(72) Inventors:
- **Pawulski, Tadeusz**
  The Woodlands, TX 77381 (US)
- **Turney, Michael A.**
  Houston, TX 77094 (US)

(74) Representative: **Mercey, Fiona Susan**
L'Air Liquide SA,
Département Propriété Intellectuelle,
75 quai d'Orsay
75321 Paris Cedex 07 (FR)

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

(57) A cryogenic distillation apparatus for the separation of air using a column system comprises at least one column (HP,LP,M) a main heat exchanger (E1), a conduit (5,11,7) for sending cooled compressed air to the main heat exchanger and from the main heat exchanger to the column system, conduits (33,19) for sending oxygen enriched, and nitrogen enriched streams from the column system to the main heat exchanger, a purge vaporizer (E2), a conduit for removing a purge stream (31) from the column system and sending the purge stream to the purge vaporizer, a conduit (13) for sending compressed and purified air (9) to the purge vaporizer and a conduit for sending compressed and purified air from the purge vaporizer to the column system.

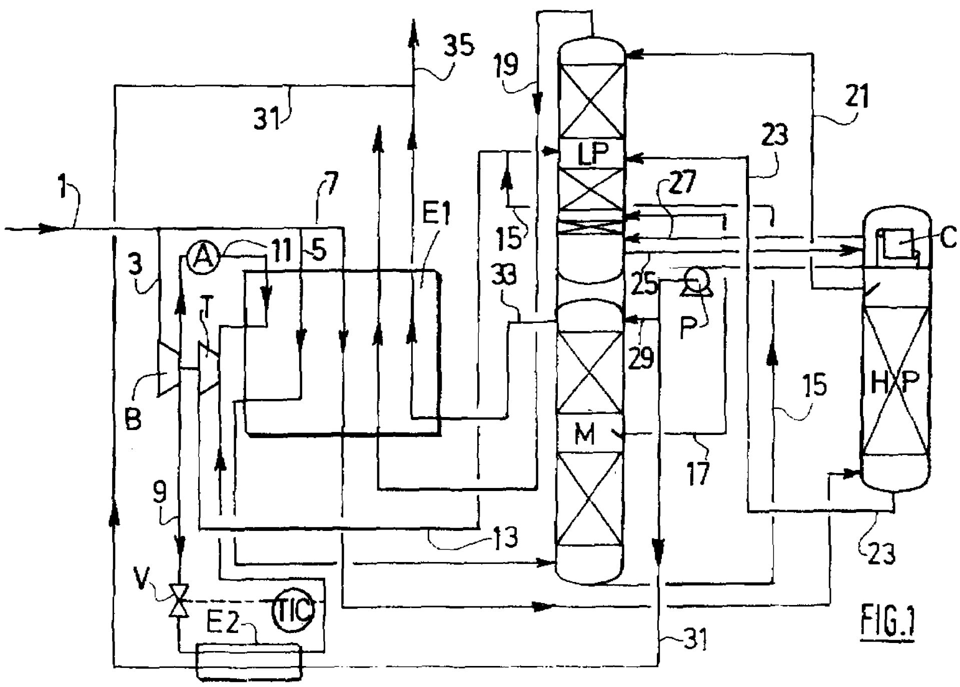

FIG.1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a process and apparatus for the separation of air by cryogenic distillation.

[0002] A cryogenic air separation unit has a distillation section where air is distilled into its heavy and light components. In this process, hydrocarbons become concentrated in the liquid oxygen stream and create a safety concern. Front-end adsorption beds of alumina and molecular sieve do not stop all these impurities from entering the distillation process.

[0003] Traditional methods of removing the remainder of impurities in the oxygen rich liquid streams include an additional adsorption step through a bed of silica gel. Another option is simply to purge a small portion of the hydrocarbon containing oxygen liquid stream to prevent accumulation of heavy impurities, and maintain its concentrations at sufficiently low levels. This option is typically only justified for small projects where the additional capital cost of the silica gel adsorption unit is high compared to the loss of refrigeration caused by purging liquid oxygen. Therefore, it is desirable to have a cost effective system, which will remove the hazardous hydrocarbons without a high loss of refrigeration caused by purging liquid oxygen. U.S. Patent 5,379,599 and US Patent 5,471,842 describe the case where the purge stream is pumped and vaporized in the main heat exchanger.

[0004] This disclosure suggests installing a small purge vaporizer exchanger, which will provide recovery of most of the refrigeration of the purged liquid stream. This exchanger vaporizes and warms the oxygen stream against a warm air stream. The warm vaporized oxygen may be either vented or remixed with the gaseous oxygen exiting the main heat exchanger as product. The warm air stream may come from the discharge of the absorbers, booster compressor, or other warm pressurized source. The flow of air is adjusted to control the temperature of the air exiting the exchanger above a specified value (--90°C) to avoid the deposit of hydrocarbons in the exchanger.

[0005] For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying drawings, in which like elements are given the same or analogous reference numbers and wherein:

- Figure 1 illustrates an air separation unit according to the invention for the production of oxygen using a side by side double column and a mixing column;
- Figure 2 illustrates Figure 2 shows an air separation unit according to the invention for the production of nitrogen using a single column.

[0006] In Figure 1, the low pressure column LP is placed above the mixing column M in a single structure with the high pressure column HP placed apart but thermally linked with the low pressure column, via condenser C.

[0007] A stream of compressed and purified air **1**, substantially at the pressure of the high pressure column HP, is sent to the cold box. It is split into three streams. The first stream **3** is not cooled, but sent to a booster compressor B, where it is compressed to a pressure substantially higher than that of the high pressure column. It is then divided into two portions **9** and **11**. Portion **9** is sent to heat exchanger E2, whilst portion **11** is cooled in after-cooler A, and then sent to main heat exchanger E1 for further cooling.

[0008] Heat exchanger E2 may be of the shell and tube type, wound tube type, or any design capable of handling large temperature gradients, and avoiding potential plugging of the exchanger passages.

[0009] Portion **9** is used to vaporize a stream of purge oxygen **31** from the condenser of the high pressure column within the heat exchanger E2. The air entering the heat exchanger E2 is at a temperature well above ambient, whereas the oxygen stream has been pumped at cryogenic temperatures. It is consequently necessary to adjust the air flow **9** so that the air leaving exchanger E2 is above a specified value (~-90°C) to avoid the deposit of hydrocarbons therein. For example a temperature indicator and controller TIC may be placed on the outlet air of exchanger E2 which controls a valve V used to change the airflow **9**.

[0010] Portion **11** is cooled to an intermediate temperature of the heat exchanger E1 and sent to turboexpander T along with the cooled air stream **9** from exchanger E2. The expanded stream of air **13** is then sent to the low pressure column LP.

[0011] Air stream **5** is cooled to an intermediate temperature of the heat exchanger E1 and then sent to the bottom of the mixing column M.

[0012] Air stream **7** flows from the warm end to the cold end of heat exchanger E1 and is then sent to the bottom of the high pressure column HP.

[0013] The columns shown illustrate a conventional mixing column set up in which liquid oxygen **29** is sent from the condenser to the top of the mixing column M, liquid nitrogen **21** is sent from the high pressure column HP to the top of the low pressure column LP and oxygen enriched liquid **23** is sent from the bottom of the high pressure column to the low pressure column. An intermediate liquid **17** and a bottom liquid **15** of the mixing column M are sent to the low pressure column LP. The bottom liquid is preferably mixed with air stream **13** before entering the column LP.

[0014] The condenser C is fed with bottom liquid **25** from the LP column and produces vaporized gaseous oxygen **27**, which is sent back to the low pressure column.

[0015] Gaseous nitrogen **19** is removed from the top of the low pressure column and warmed in heat exchanger E1.

[0016] Gaseous oxygen **33** from the top of the mixing column M is sent to the heat exchanger E1, warmed up to the warm end, and mixed with vaporized oxygen **31** from heat exchanger E2 to form the product oxygen stream **35**.

It is important to have sufficient pressure drop available for the air stream to go through the purge vaporizer E2, control valve V, and piping before mixing back into the process. If the available pressure drop is too low, it may not be possible to achieve enough air flow through the purge vaporizer and it will not work properly. On the other hand, if too much pressure drop is taken (e.g. by taking medium pressure air and returning to the low pressure circuit after the turbine) then the reduction in turbine flow will yield a loss of refrigeration and reduce the refrigeration benefit of the purge vaporizer.

[0017] If the air is taken from the discharge of a booster compressor but before its aftercooler, it can be injected back into the inlet of the turbine, such that refrigeration is not lost (See Figure 1). For this case, the air stream essentially bypasses the aftercooler and warm section of the main exchanger. This yields enough pressure drop for the purge vaporizer and control valve, since the booster aftercooler typically takes significant pressure drop.

[0018] If the air stream is taken from upstream of the booster compressor (if any) it is typically returned to the air stream at the cold end of the main exchanger. In this case the vaporized purge stream is returned to the inlet of the waste oxygen expander to minimize refrigeration loss.

[0019] The air separation unit of Figure 2 uses a single column with a double top reboiler. In Figure 2, a compressed purified air stream **1** is divided in two forming air stream **9** and air stream **5**. Air stream **5** is sent to heat exchanger E1 in which it cools, and is then sent to the bottom of the column HP. Air stream **9** is sent to heat exchanger E2 without passing into heat exchanger E1. It is then mixed with cooled air stream **5** and sent to the column HP.

[0020] Oxygen enriched liquid **15** from the bottom of the column is subcooled in exchanger E3 and sent to condenser C1. Condenser C1 serves to condense part of the gaseous nitrogen at the top of the column thereby vaporizing part of the oxygen enriched liquid. The vaporized oxygen enriched liquid is sent to a booster B and returned to the column at a point below the entry point of stream **5**.

[0021] The oxygen enriched liquid which is not vaporized in C1 is sent to condenser C2 situated underneath condenser C1. Condenser C2 also serves to condense part of the gaseous nitrogen at the top of the column, thereby vaporizing part of the rest of the oxygen enriched liquid. The oxygen enriched liquid purge not vaporized in C2 is removed as stream **31** and is vaporized in exchanger E2 against the air stream **9**. The vaporized purge stream is expanded in turbine T, which drives booster B, used to subcool the oxygen enriched liquid in exchanger E2, warmed in exchanger E1 and removed from the system as stream **53**.

[0022] Product nitrogen **33** is removed from the top of the column and warmed in heat exchanger E1. Medium purity nitrogen **19** is removed from the middle of the column and warmed in heat exchanger E1. Liquid nitrogen **51** is removed from the top of the column and sent to storage S.

[0023] It will be appreciated that the invention may be applied in other types of air separation unit, such as single column units, double column units, and double column units incorporating other columns, such as argon columns and triple column units. In general, this applies to any plant that needs to purge heavy components and recover the refrigeration and/or molecules of the purge stream. The purge is taken from the sump of the vaporizer or column, which contains the highest concentration of heavy components (e.g. hydrocarbons). The essential characteristics of the present invention are described completely in the foregoing disclosure. One skilled in the art can understand the invention and make various modifications without departing from the spirit of the invention and without deviating from the scope and equivalents of the claims, which follow.

Claims

1. A cryogenic distillation air separation process using a column system comprising at least one column including the steps of:

   a) compressing feed air in a compressor to produce compressed air;
   b) purifying compressed air in a purification unit to produce compressed and purified air;
   c) sending compressed and purified air to a main heat exchanger to produce cooled, compressed and purified air;
   d) sending cooled, compressed and purified air to the column system;
   e) withdrawing nitrogen enriched and oxygen enriched fluids from the column system and warming the nitrogen enriched and oxygen enriched fluids in the main heat exchanger;
   f) withdrawing a liquid purge stream from the column system; and
   g) without having previously warming the liquid purge stream in the main heat exchanger, vaporizing the liquid purge stream by heat exchange with a stream of fluid at a temperature of above 0°C.

2. Process according to Claim 1, wherein the stream of fluid at a temperature of above 0°C is an air stream.

3. Process according to Claim 2, wherein the air stream is removed downstream of the compressor.

4. Process according to Claim 3, wherein the air stream is removed downstream of the purification unit.

5. Process according to Claim 4, wherein the air stream is removed downstream of a booster compressor.

6. Process according to Claim 1, wherein the liquid purge stream is vaporized in a heat exchanger separate from the main heat exchanger.

7. Process according to Claim 6, wherein the amount of air sent to the heat exchanger is controlled to maintain the temperature of the cooled air leaving the heat exchanger above a given temperature.

8. Cryogenic distillation apparatus for the separation of air using a column system, comprising at least one column further comprising:

a) a main heat exchanger;
b) a conduit for sending cooled compressed air to the main heat exchanger, and from the main heat exchanger to the column system;
c) conduits for sending oxygen enriched and nitrogen enriched streams from the column system to the main heat exchanger;
d) a purge vaporizer;
e) a conduit for removing a purge stream from the column system and sending the purge stream to the purge vaporizer;
f) a conduit for sending compressed and purified air to the purge vaporizer; and
g) a conduit for sending compressed and purified air from the purge vaporizer to the column system.

9. Apparatus according to Claim 8, wherein the purge vaporizer is a heat exchanger of the wound type or of the shell and tube type.

10. Apparatus according to Claim 8, wherein the main heat exchanger is of the plate fin type.

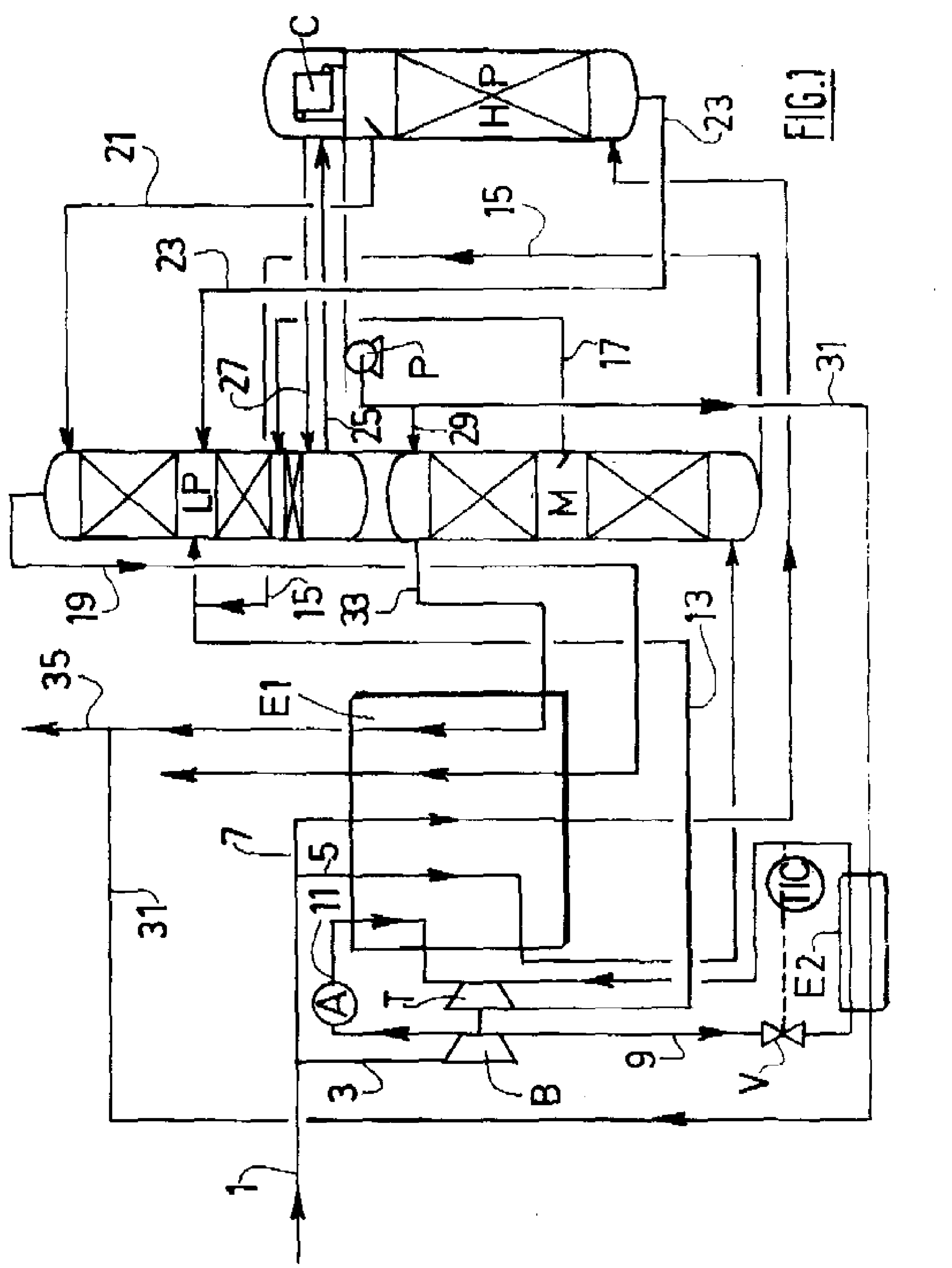

FIG.1

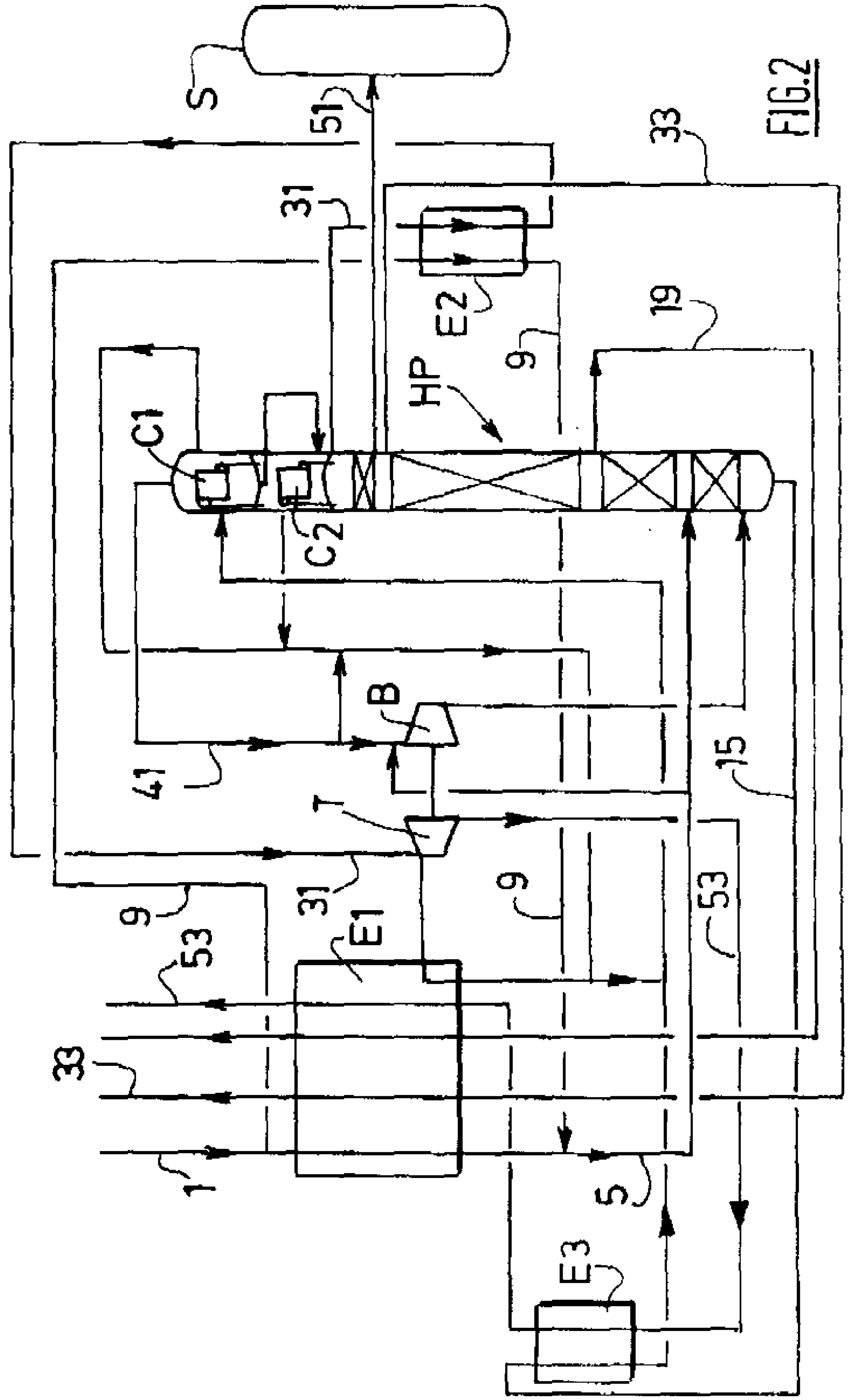

FIG.2

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5379599 A **[0003]**
- US 5471842 A **[0003]**