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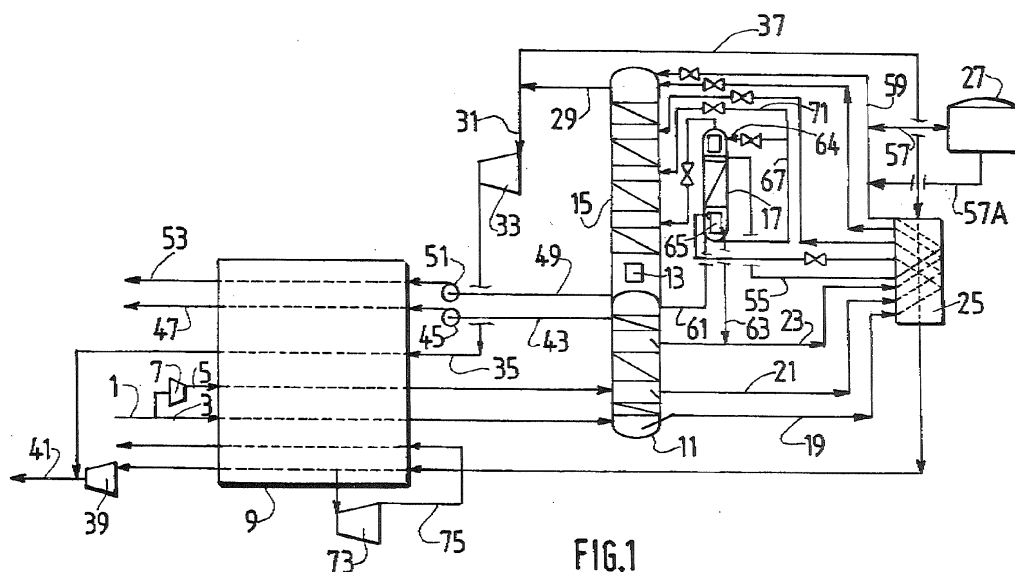
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• **Davidian, Benoit****94100 SAINT MAUR DES FOSSES (FR)**(54) **Process for the separation of air by cryogenic distillation**

(57) A process for the separation of air by cryogenic distillation operates either with a product ratio greater than 2.5 in which case nitrogen enriched liquid is sent from a storage tank (27) to the column system and feed air or nitrogen enriched gas (29) from the column system is compressed in a first compressor (33) having an inlet temperature of less than -50°C and then sent to the heat

exchanger, or with a product ratio less than 2.5 in which case a second nitrogen rich gas removed from the column system is expanded in a turbine (73) having an inlet temperature lower than the ambient temperature or liquefied in a liquefier and nitrogen enriched liquid (57) is sent to the storage tank from the outlet of the turbine and/or from the column system and/or from the liquefier.

**FIG.1****EP 2 713 128 A1**

Description

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

[0002] The Integrated Gasified Combined Cycle is usually selected to generate clean energy from coal. This clean energy production technique is especially suited for new coal-based power generation projects specified to operate efficiently and with minimal pollution to the environment.

[0003] To gasify the coal for the IGCC, impure high pressure oxygen is used. In addition, nitrogen is generally required in a relatively pure state at quite high pressure in the combustion of the synthesis gas in the gas turbine to dilute the synthesis gas or hydrogen produced during the gasification process, so as to reduce the nitrous oxides (NOx) emission levels.

[0004] To produce oxygen for an IGCC plant, three well known techniques used in the context are:

- producing the oxygen in an independent ASU (air separation unit),
- taking air for the ASU from the gas turbine compressor,
- taking part of the air for the ASU from the gas turbine compressor and using a dedicated compressor to produce the rest.

[0005] The types of gasification or gas turbine would dictate the required quantity of nitrogen to be used in the IGCC complex. It can be seen from this characteristic that the air separation unit ASU for the IGCC is a combination of an oxygen plant and a nitrogen generator plant.

[0006] The air separation process frequently used for this type of application is the elevated pressure process. Although air separation units operating with this concept have good energy efficiency and reduced power consumption, it is not always possible to use this sort of ASU because the nitrogen/oxygen ratio is generally fixed at a value close to that found for air, ie close to 3.6. If the required ratio is lower than this value, for example about 2.5.

[0007] An object of the present invention is to provide an air separation unit with reduced energy consumption but which is capable of producing nitrogen and oxygen with a nitrogen/oxygen ratio of less than 3.6, preferably greater than 4.

[0008] According to one object of the invention, there is provided a process for the separation of air by cryogenic distillation in which air is purified, cooled in a heat exchanger and separated in a column system including at least a first column and a second column, the first column operating at a higher pressure than the second column and the top of the first column being thermally linked to the bottom of the second column via a first re-boiler-condenser, oxygen enriched liquid is removed from the first column and sent to the second column or

liquid derived from the oxygen enriched liquid is sent to the second column, nitrogen enriched liquid is removed from the first column and sent to the second column, oxygen rich liquid is removed from the second column, pressurized and vaporized in the heat exchanger to form an oxygen rich gas, nitrogen rich fluid is removed from the column system and warmed in the heat exchanger to form a first nitrogen rich gas, wherein

- i) during a first period, the product ratio, being the ratio between the amount of nitrogen rich gas produced and the amount of oxygen rich gas produced, is greater than 2.5, nitrogen enriched liquid is sent from a storage tank to the column system and feed air or nitrogen enriched gas from the column system is compressed in a first compressor having an inlet temperature of less than -50°C and then sent to the heat exchanger, and
- ii) during a second period, the product ratio is less than 2.5 and a second nitrogen rich gas removed from the column system is expanded in a turbine having an inlet temperature lower than the ambient temperature or liquefied in a liquefier and nitrogen enriched liquid is sent to the storage tank from the outlet of the turbine and/or from the column system and/or from the liquefier.

[0009] According to other optional features:

- during the first period the product ratio is greater than 3.
- during the second period the product ratio is less than 2.
- during the first period, nitrogen enriched gas is removed from the second column, compressed in the first compressor without having been warmed and sent to the heat exchanger.
- during the second period, the nitrogen rich gas removed from the column system is warmed in the heat exchanger expanded in the turbine and then warmed in the heat exchanger.
- the turbine has an inlet temperature of at most -50°C, preferably of at most -100°C.
- during the second period, the outlet pressure of the turbine is substantially equal to the pressure of the second column.
- no nitrogen rich gas is sent to the turbine during the first period.
- no gas is sent to the first compressor during the second period.
- the price of electricity is greater in the second period than in the first period.
- the first compressor does not operate during the second period.
- no nitrogen enriched liquid is sent to the storage tank during the first period.
- during the second period at least one cryogenic liquid is withdrawn from the process as a final product and

preferably during the first period the same cryogenic liquid is not withdrawn from the process as a final product.

- the second column operates at a pressure of at least 2 bars abs and the nitrogen rich gas expanded in the turbine is removed from the second column.
- the nitrogen rich gas expansion turbine does not operate during the first period.
- the first compressor compresses nitrogen enriched gas from the column system, preferably from the second column, and a second compressor compresses the first nitrogen rich gas from the column system downstream of the heat exchanger, the outlet pressures of the first and second compressors being substantially the same.
- the column system includes a third column operating at an intermediate pressure.
- the second column has a second reboiler-condenser at an intermediate position thereof.
- the oxygen rich gas is sent to a gasifier of an IGCC system.
- the first nitrogen rich gas is used to dilute synthesis gas or hydrogen sent to the gas turbine of an IGCC system.
- the first period corresponds to a period when the electricity production of the IGCC system is above a given level and the second period corresponds to a period when that electricity production is below the given level.

[0010] The invention will be described in greater detail with reference to Figures 1 to 3 which represent processes according to the invention.

[0011] Figure 1 shows a cryogenic air separation process using a standard double column, having a first column 11 and a second column 15, the first column operating at a higher pressure than the second column and being placed below the second column. The top of the first column 11 is thermally linked to the bottom of the second column 15 by means of a vaporizer-condenser 13 placed at the bottom of the second column 15. It is also possible for the second column to use an intermediate vaporizer-condenser (not illustrated).

[0012] The process also uses an intermediate pressure column 17 having a bottom reboiler 65 and a top condenser. The presence of the column 17 is not essential.

[0013] When the process is in operation, an air stream 1 compressed to the operating pressure of the first column 11 is divided into two parts. One part 3 is cooled in heat exchanger 9 and sent in gaseous form to the first column 11. The other part 5 is boosted to a higher pressure by booster compressor 7 and sent to the heat exchanger 7. The boosted air 5 is cooled in the heat exchanger 9 and sent to the first column 11 after expansion in liquid or partially condensed form.

[0014] When the process is in operation, oxygen enriched liquid 19 from the bottom of the first column 11 is

sent to subcooler 25 and then expanded into the column 17. Liquid 67 from the bottom of column 17 is sent to the top condenser as stream 64, where it is partially evaporated, the liquid and gas streams formed being sent to the second column 15. Part 71 of the liquid is sent from the bottom of column 17 to the second column 15. A liquid stream 21 is removed from an intermediate region of the first column and expanded into the second column 15. Alternatively at least part of stream 5 can be sent directly to the second column 15. A first nitrogen enriched liquid stream is sent as stream 23 from the first column to the second column, being removed a few trays below the top of the first column. A nitrogen enriched gas stream 61 is removed at the top of the first column, condensed in bottom condenser 65 and mixed with stream 23 as stream 63.

[0015] A liquid stream 55 from the top of column 17 is sent to the top of column 15.

[0016] The column system produces a high pressure gaseous oxygen stream 53 by removing liquid oxygen 49 from the bottom of second column 15, pressurizing it via pump 51 and vaporizing the pumped liquid in exchanger 9.

[0017] The column system produces a high pressure gaseous nitrogen stream 47 by removing liquid nitrogen 43 from the top of first column 11, pressurizing it via pump 45 and vaporizing the pumped liquid in exchanger 9.

[0018] These pressurized streams may be sent to a gasifier.

[0019] To provide refrigeration for the process, gaseous nitrogen 29, 37 is removed at the top of the second column 15, warmed in subcooler 25, partially warmed in heat exchanger 9 and sent as stream 75 to a turbine 73 having an inlet temperature which is an intermediate temperature of the heat exchanger 9. The expanded nitrogen is sent to the cold end of the exchanger and warmed as far as the warm end. The nitrogen 75 forms a waste stream.

[0020] Another part of the nitrogen 37 is warmed in the heat exchanger to the warm end, compressed in compressor 39 and sent to a gas turbine via conduit as stream 41.

[0021] All of the foregoing steps take place whenever the process operates.

[0022] In order to increase the relative amount of gaseous nitrogen produced, the process uses two particular special operations during two periods.

[0023] During the first period, the ratio between the amount of nitrogen rich gas produced 41 and the amount of oxygen rich gas 53 produced (known as the "product ratio"), is greater than 2.5. Nitrogen enriched liquid 57A is sent from a storage tank 27 to the column system 11, 15 and nitrogen enriched gas 29, 31 from the second column 15 of the column system is compressed in a compressor 33 having an inlet temperature of less than -50°C and then sent to the cold end of the heat exchanger 9. Preferably the compressor 33 only operates when nitrogen enriched liquid 57A is sent to the column. The gas 31 is

then warmed in the heat exchanger and mixed with the gas from compressor 39 to form stream 41. Either no nitrogen is sent to the turbine 73 or some nitrogen may be sent to the turbine 73.

[0024] During a second period, the product ratio is less than 2.5 and a nitrogen rich gas removed from the column system is expanded in a turbine 73 having an inlet temperature lower than the ambient temperature and nitrogen enriched liquid 57 is sent to the storage tank 27 from the column system. No nitrogen is sent to the compressor 33 and all of stream 29 is removed as stream 37.

[0025] Figure 2 shows a variant of Figure 1 in which the cold turbine 73 is replaced by a liquefier. In this case, during the first period, the ratio between the amount of nitrogen rich gas produced 41 and the amount of oxygen rich gas 53 produced (known as the "product ratio"), is greater than 2.5. Nitrogen enriched liquid 57A is sent from a storage tank 27 to the column system 11, 15 and nitrogen enriched gas 29, 31 from the second column 15 of the column system is compressed in a compressor 33 having an inlet temperature of less than -50°C and then sent to the cold end of the heat exchanger 9. Preferably the compressor 33 only operates when nitrogen enriched liquid 57A is sent to the column. The gas 31 is then warmed in the heat exchanger and mixed with the gas from compressor 39 to form stream 41.

[0026] During a second period, the product ratio is less than 2.5 and a nitrogen rich gas removed from the column system 37 is warmed as far as the warm end of exchanger 9. Then part of the gas is sent to compressor 39 and the rest 75 is compressed by compressor 101 and divided into two. One part 79 is cooled and liquefied in exchanger 109 to form a partially condensed stream. This stream separates in a phase separator and the liquid formed serves as final product 83. The gas 85 is sent back to the exchanger, warmed and sent to the atmosphere. The other part of gas from compressor 101 is further compressed in boosters 103, 105, is cooled in exchanger 109 and is expanded in a turbine 73 having an inlet temperature lower than the ambient temperature. The expanded gas is warmed in the exchanger 109 to an intermediate temperature and divided into two. One part 81 is expanded at the intermediate temperature in turbine 173 and rewarmed in the exchanger before being sent to the atmosphere. The rest 79 is warmed and recycled upstream of compressor 101.

[0027] No nitrogen is sent to the compressor 33 and all of stream 29 is removed as stream 37.

[0028] The process of Figure 3 differs from that of Figure 2 in that the nitrogen 75 for the liquefier is taken downstream of compressor 39, so that compressor 101 is no longer required. Part 79 of the gas from turbine 73 is recycled to a point upstream of compressor 39.

Claims

1. Process for the separation of air by cryogenic distil-

lation in which air is purified, cooled in a heat exchanger (9) and separated in a column system (11, 15, 17) including at least a first column (11) and a second column, the first column operating at a higher pressure than the second column and the top of the first column being thermally linked to the bottom of the second column via a first reboiler-condenser (13), oxygen enriched liquid (19) is removed from the first column and sent to the second column or liquid (67) derived from the oxygen enriched liquid is sent to the second column, nitrogen enriched liquid (23, 61) is removed from the first column and sent to the second column, oxygen rich liquid (49) is removed from the second column, pressurized and vaporized in the heat exchanger to form an oxygen rich gas, nitrogen rich fluid (43) is removed from the column system and warmed in the heat exchanger to form a first nitrogen rich gas, wherein

i) during a first period, the product ratio, being the ratio between the amount of nitrogen rich gas produced and the amount of oxygen rich gas produced, is greater than 2.5, nitrogen enriched liquid is sent from a storage tank (27) to the column system and feed air or nitrogen enriched gas (29) from the column system is compressed in a first compressor (33) having an inlet temperature of less than -50°C and then sent to the heat exchanger, and

ii) during a second period, the product ratio is less than 2.5 and a second nitrogen rich gas removed from the column system is expanded in a turbine (73) having an inlet temperature lower than the ambient temperature or liquefied in a liquefier and nitrogen enriched liquid (57) is sent to the storage tank from the outlet of the turbine and/or from the column system and/or from the liquefier.

2. Process according to Claim 1 wherein during the first period the product ratio is greater than 3.

3. Process according to Claim 1 wherein during the second period the product ratio is less than 2.

4. Process according to any preceding claim wherein during the first period, nitrogen enriched gas is removed from the second column (15), compressed in the first compressor (33) without having been warmed and sent to the heat exchanger (9).

5. Process according to any preceding claim wherein during the second period, the nitrogen rich gas removed from the column system is warmed in the heat exchanger (9) expanded in the turbine (73) and then warmed in the heat exchanger.

6. Process according to any preceding claim wherein

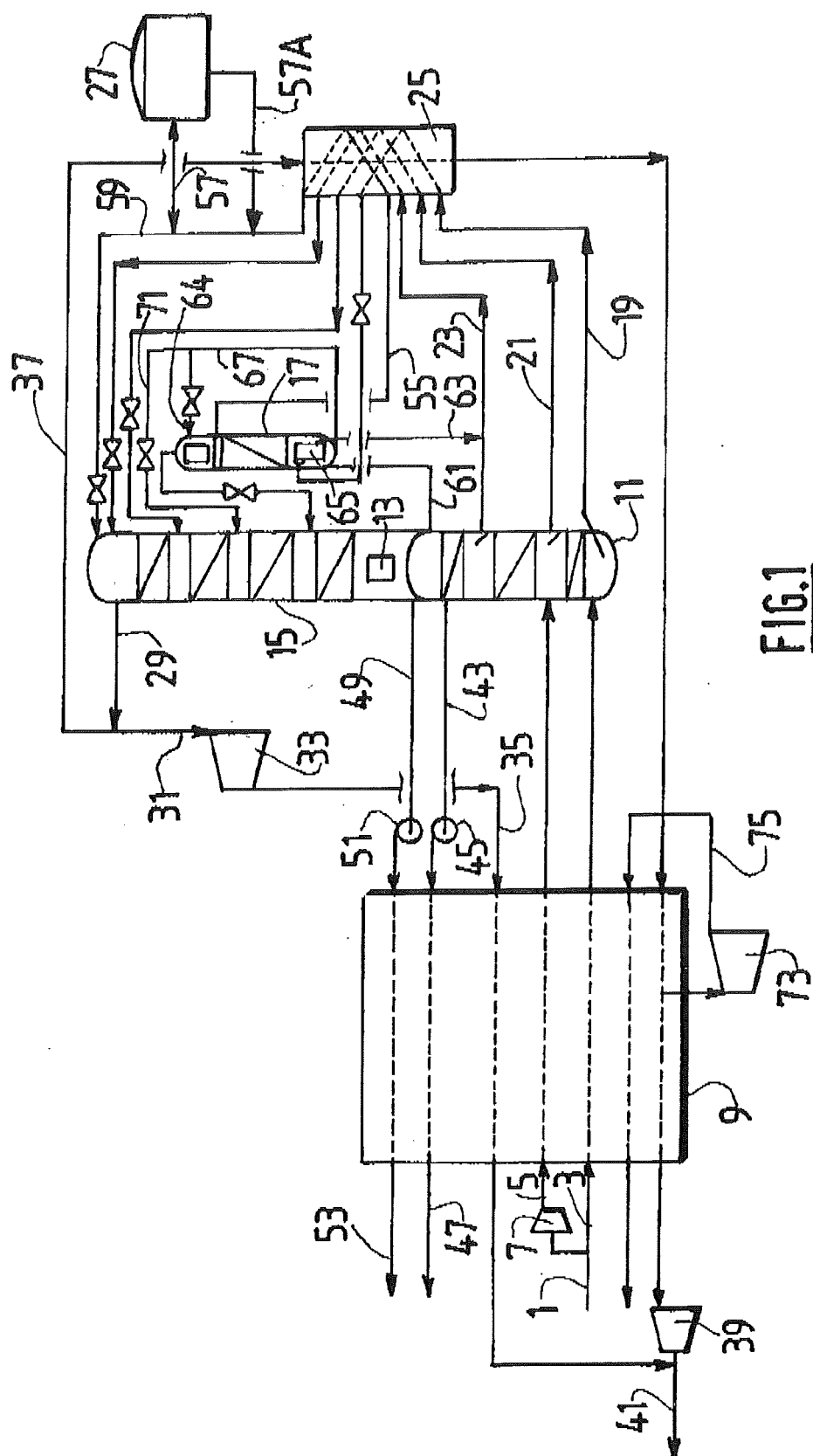
the turbine (73) has an inlet temperature of at most -50°C, preferably of at most -100°C.

7. Process according to any preceding claim wherein during the second period, the outlet pressure of the turbine (73) is substantially equal to the pressure of the second column (15). 5
8. Process according to any preceding claim wherein no nitrogen rich gas is sent to the turbine (73) during the first period. 10
9. Process according to any preceding claim wherein no gas is sent to the first compressor (33) during the second period. 15
10. Process according to any preceding claim where the price of electricity is greater in the second period than in the first period. 20
11. Process according to any preceding claim where the first compressor (33) does not operate during the second period.
12. Process according to any preceding claim wherein no nitrogen enriched liquid is sent to the storage tank (27) during the first period. 25
13. Process according to any preceding claim wherein during the second period at least one cryogenic liquid (83) is withdrawn from the process as a final product and preferably during the first period the same cryogenic liquid is not withdrawn from the process as a final product. 30
14. Process according to any preceding claim wherein the second column (15) operates at a pressure of at least 2 bars abs and the nitrogen rich gas expanded in the turbine (73) is removed from the second column. 35
15. Process according to any preceding claim wherein the nitrogen rich gas expansion turbine (73) does not operate during the first period. 40

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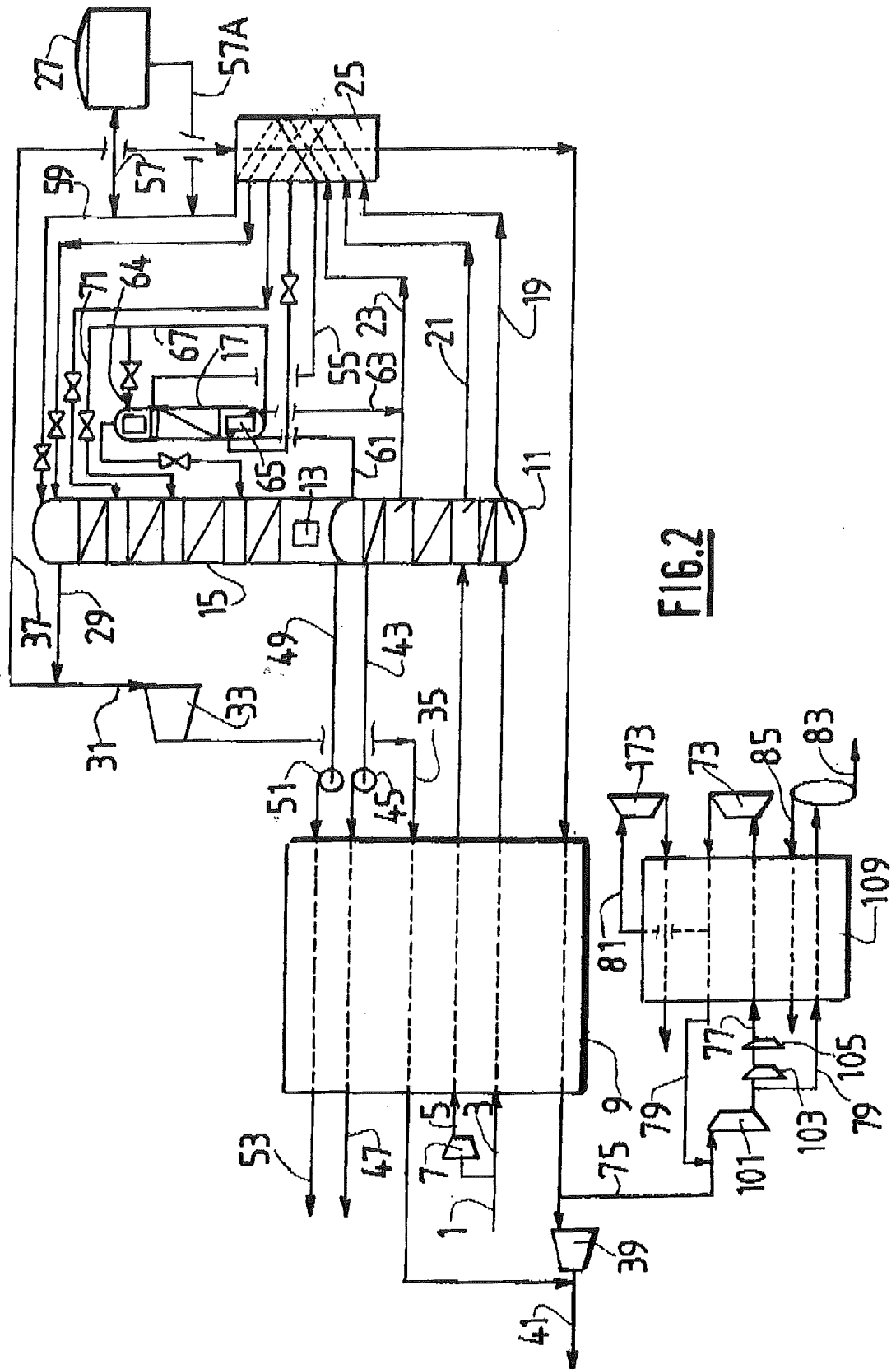


FIG. 2

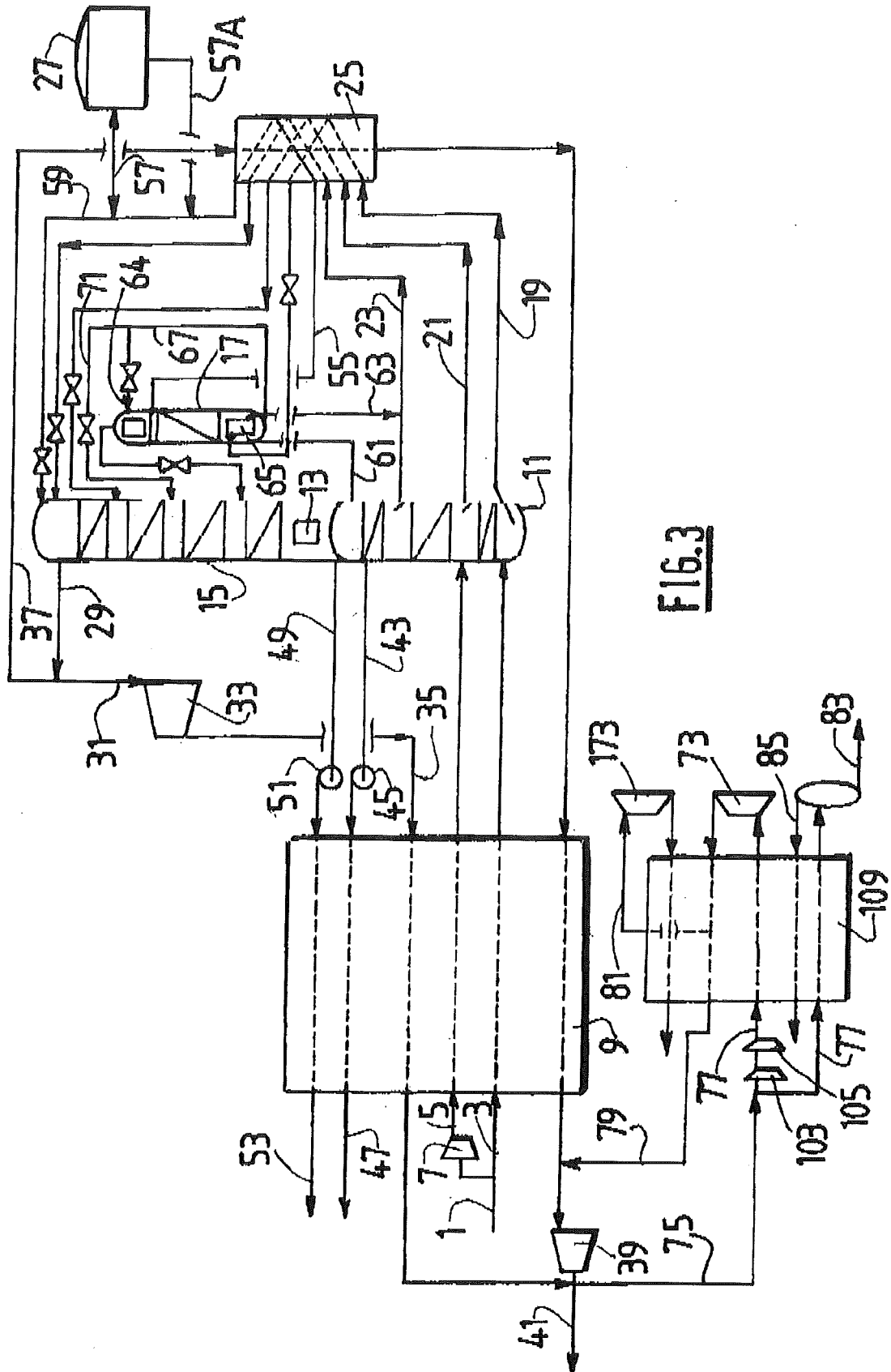


FIG. 3



EUROPEAN SEARCH REPORT

Application Number
EP 12 30 6195

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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 14 March 2013	Examiner Göriz, Dirk
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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