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(54) **CO₂ RECOVERY METHOD USING CRYO-CONDENSATION**

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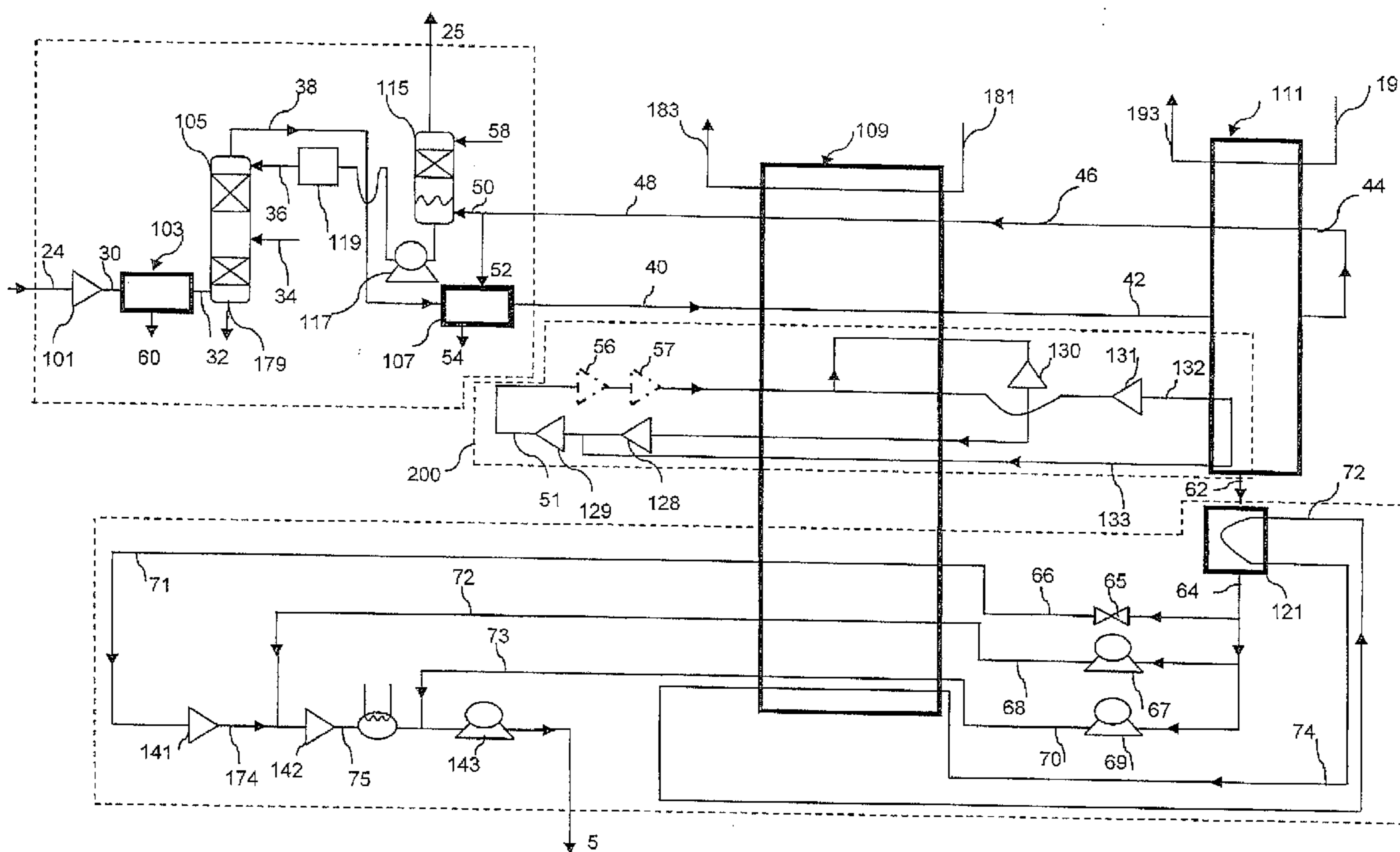
(57) **ABSTRACT**

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The present invention relates to a method of capturing carbon dioxide in a fluid comprising at least one compound more volatile than carbon dioxide CO₂, for example methane CH₄, oxygen O₂, argon Ar, nitrogen N₂, carbon monoxide CO, helium He and/or hydrogen H₂.



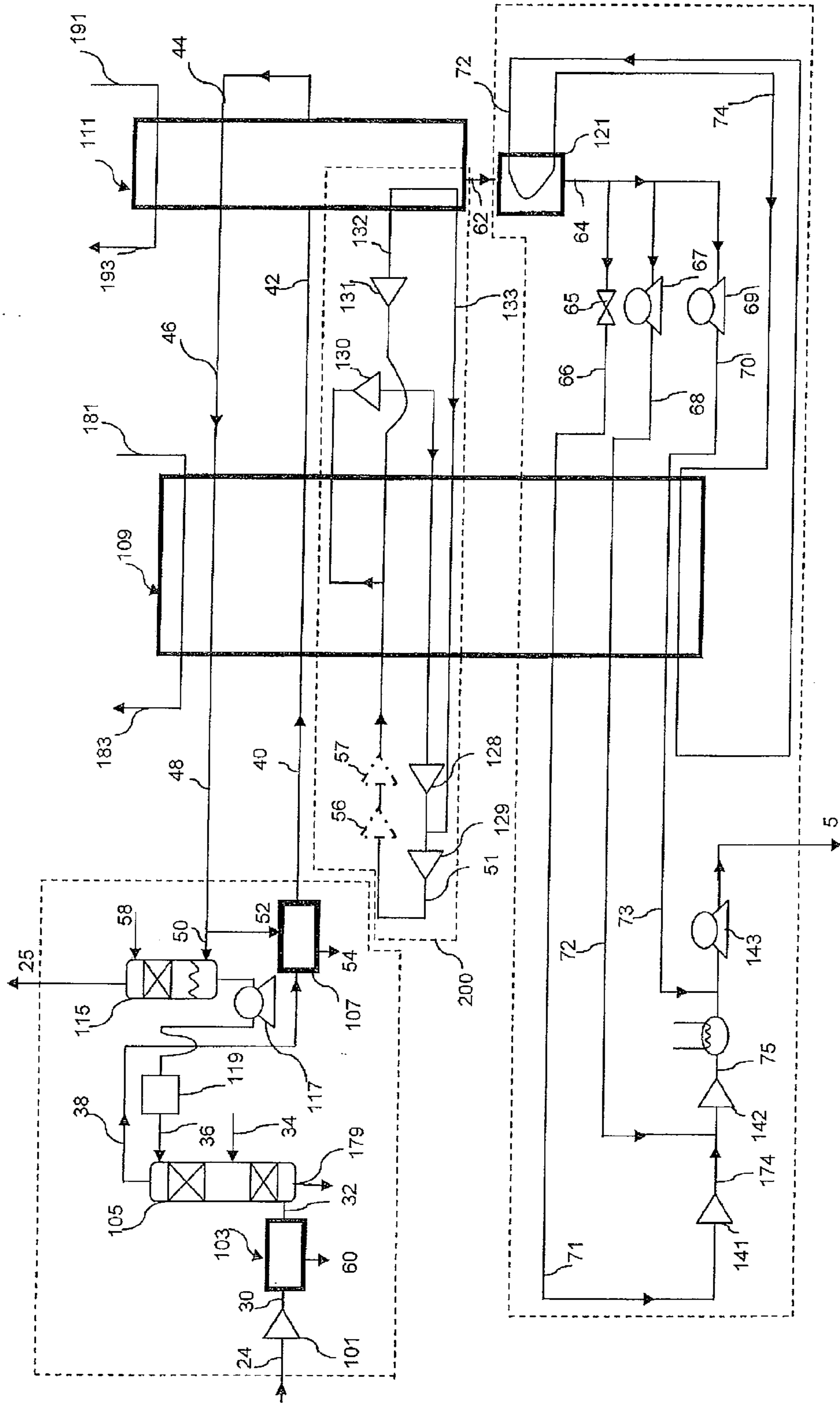


FIG. 1

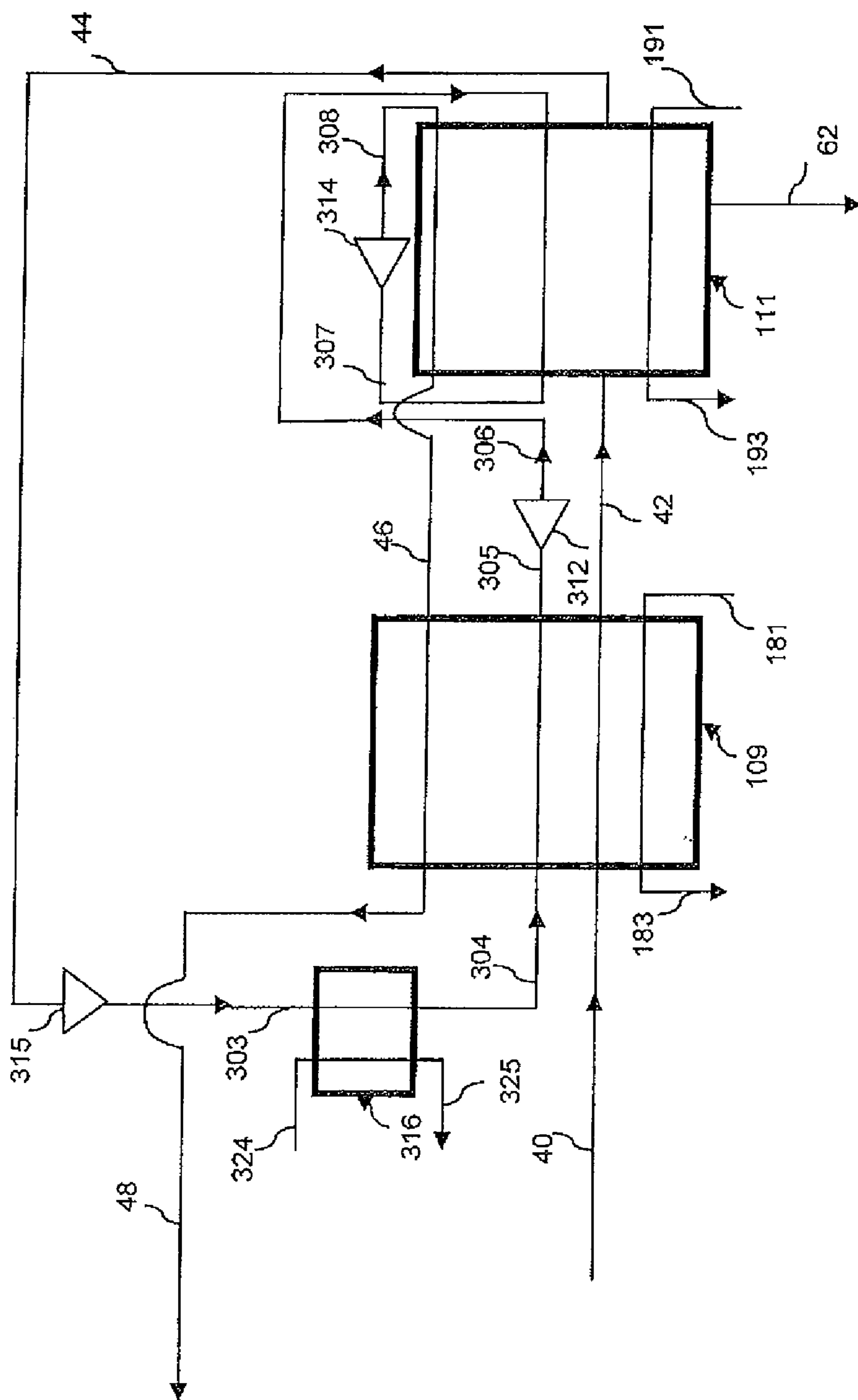


FIG. 2

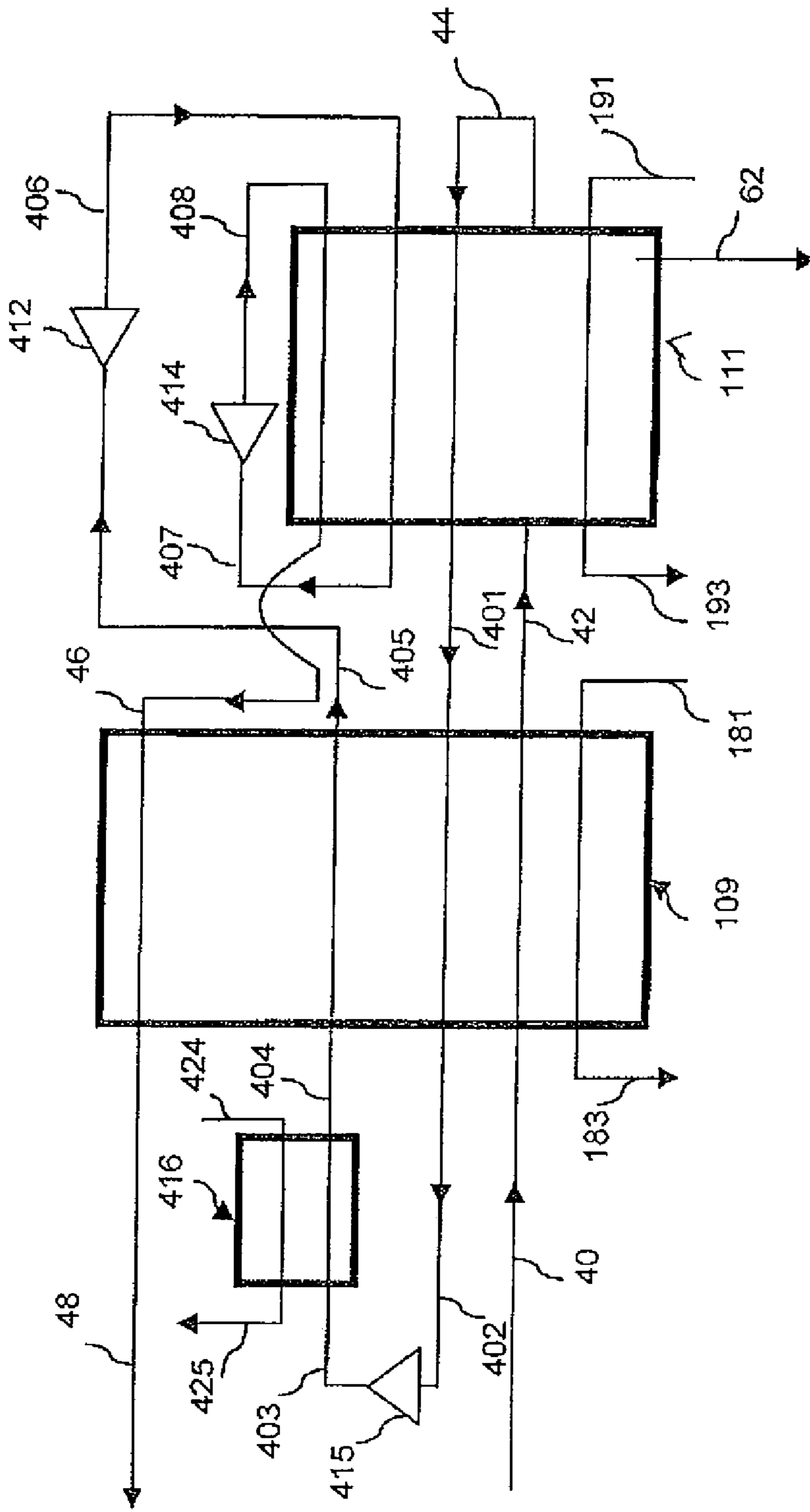


FIG. 3

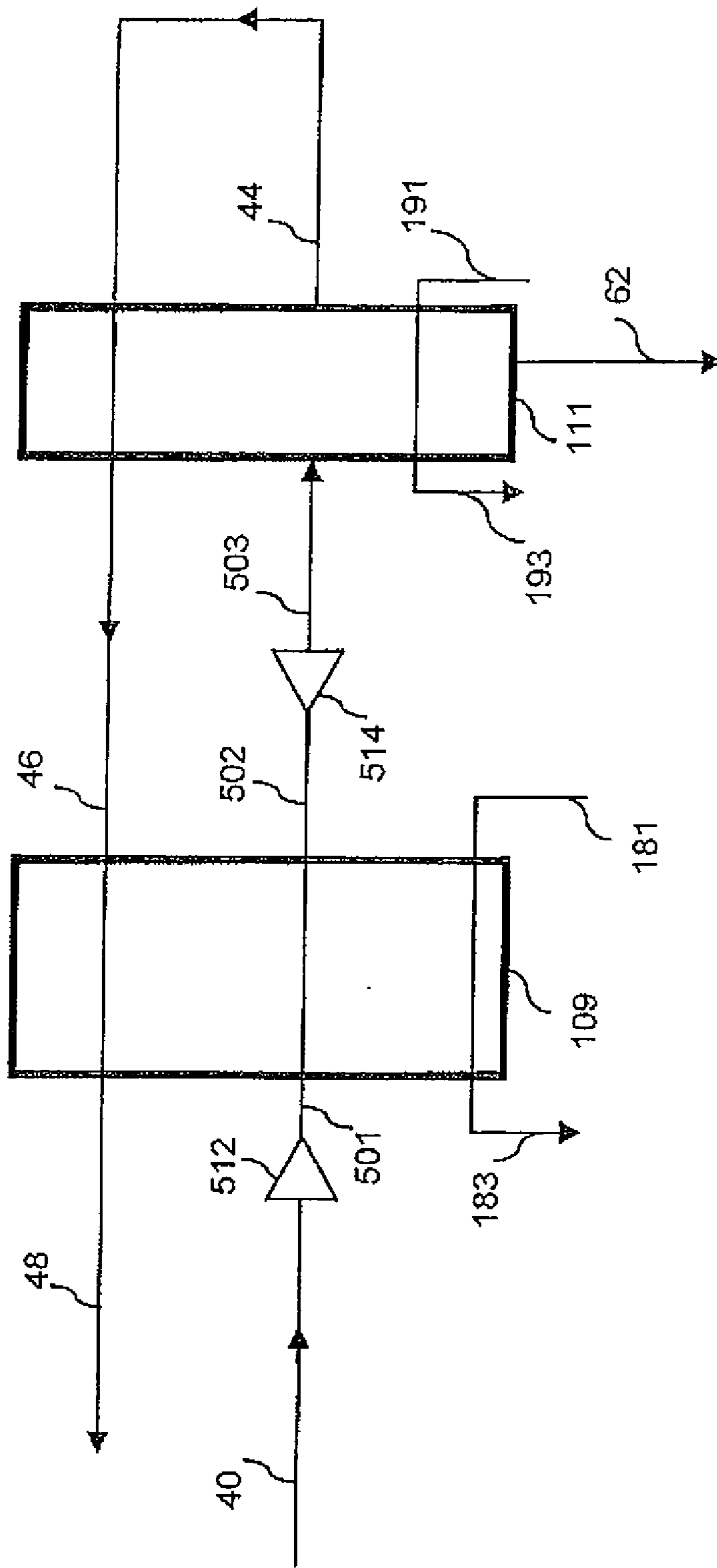


FIG. 4

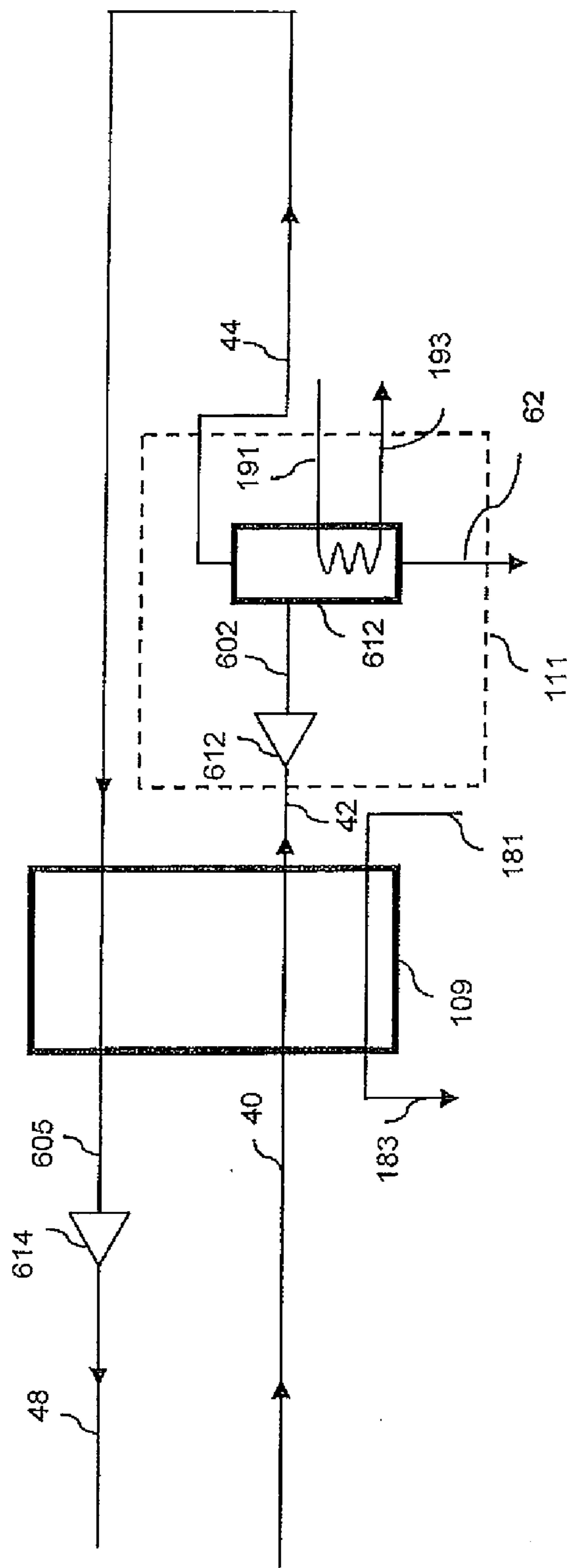


FIG. 5

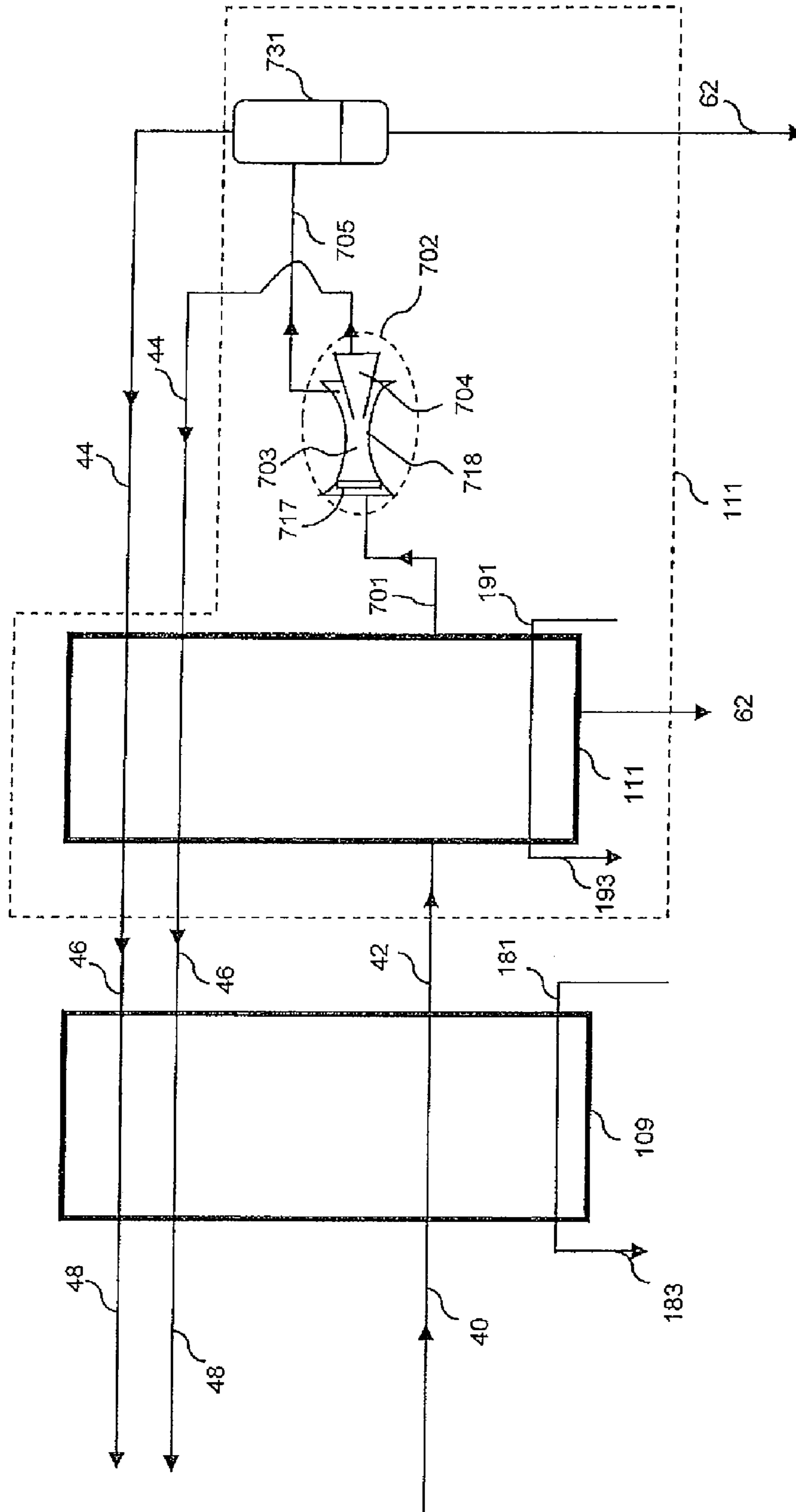


FIG. 6

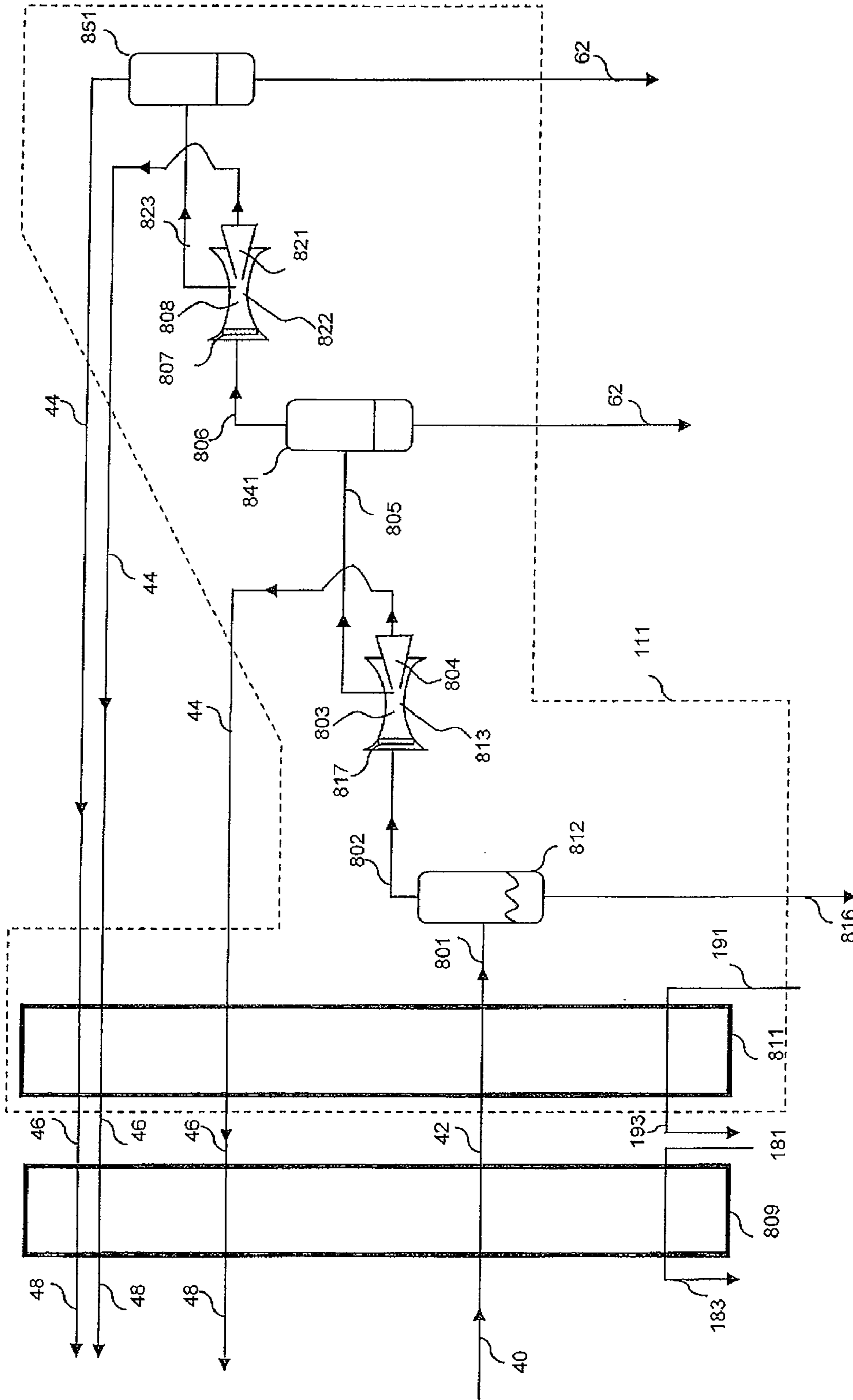


FIG. 7

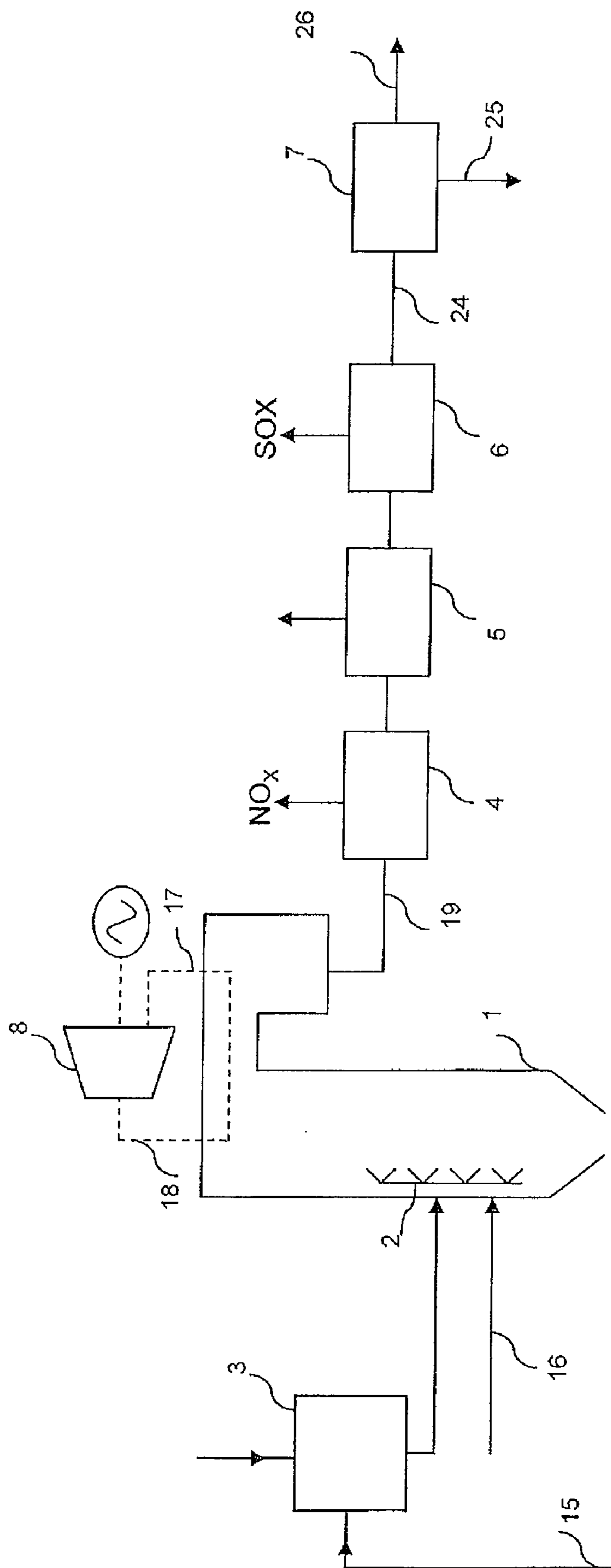


FIG. 8

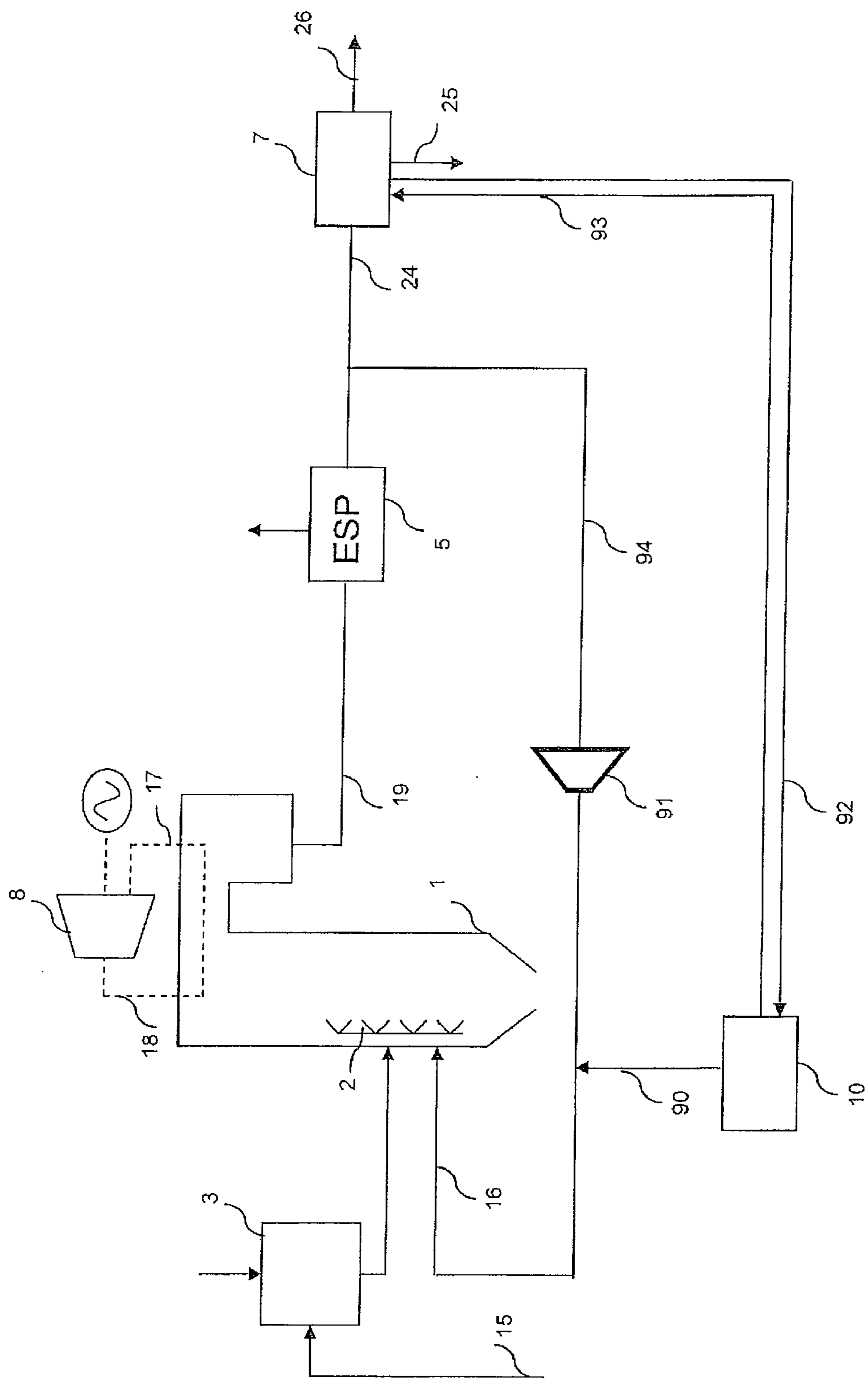


FIG. 9

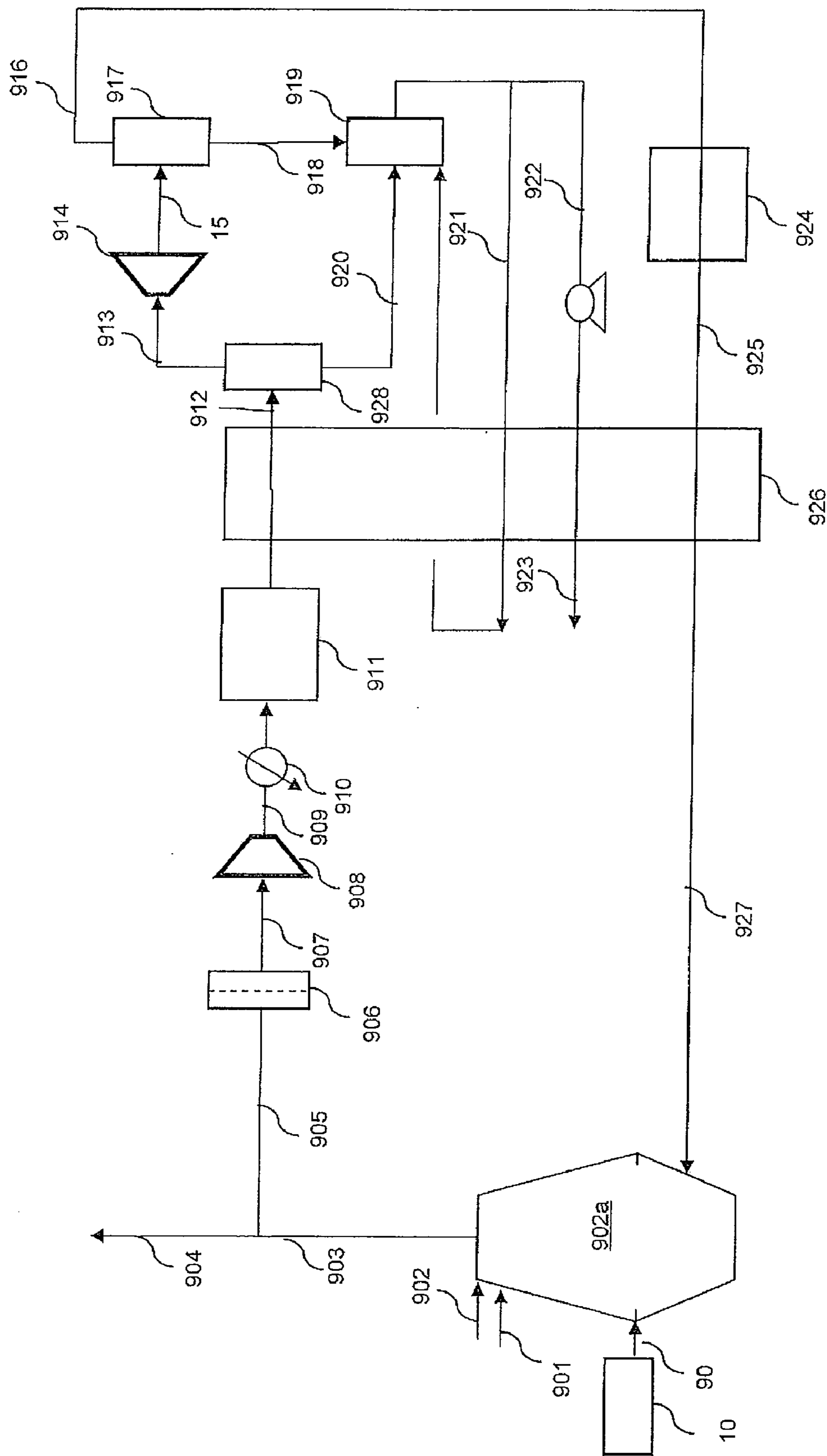


FIG. 10

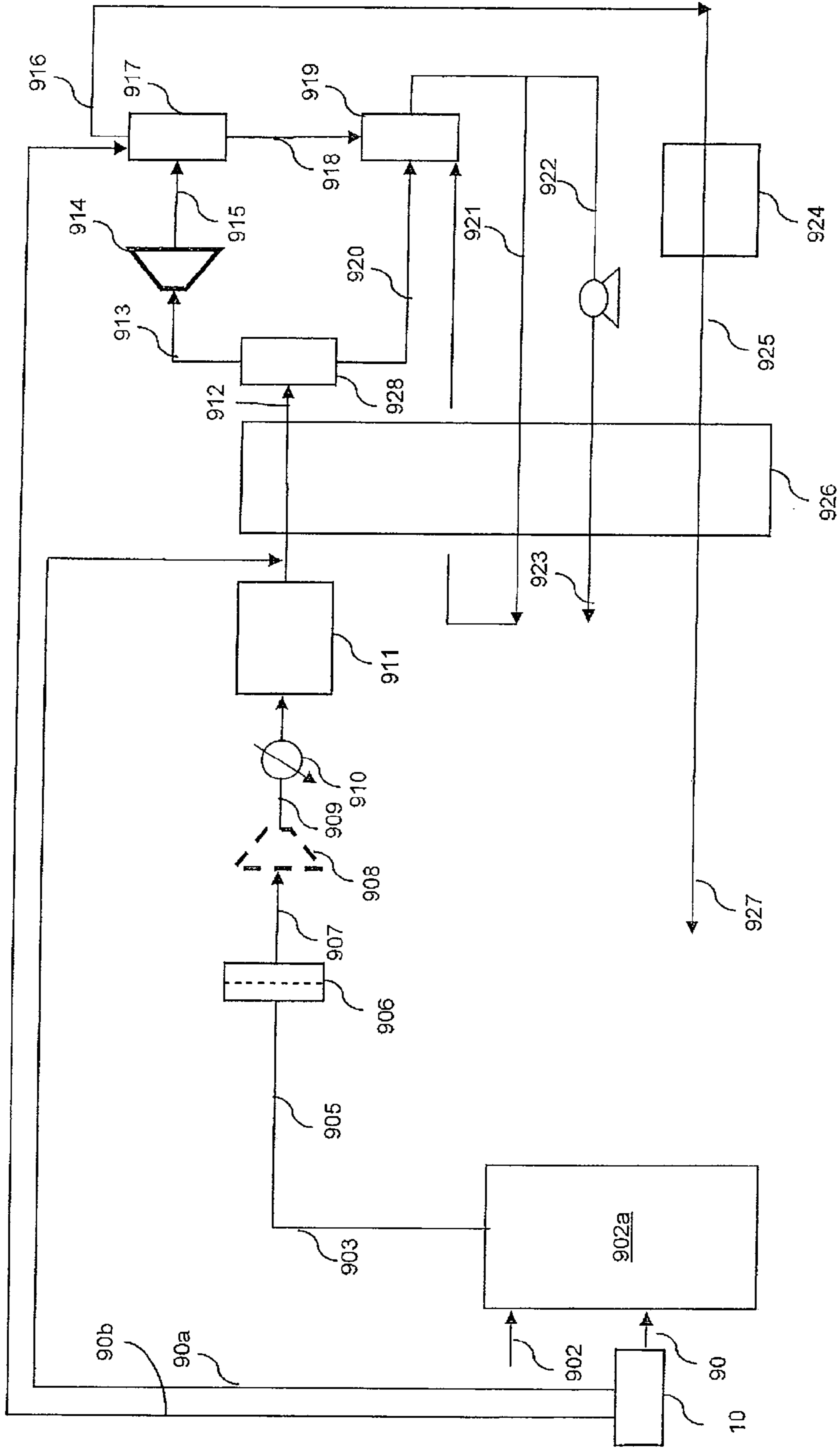


FIG. 11

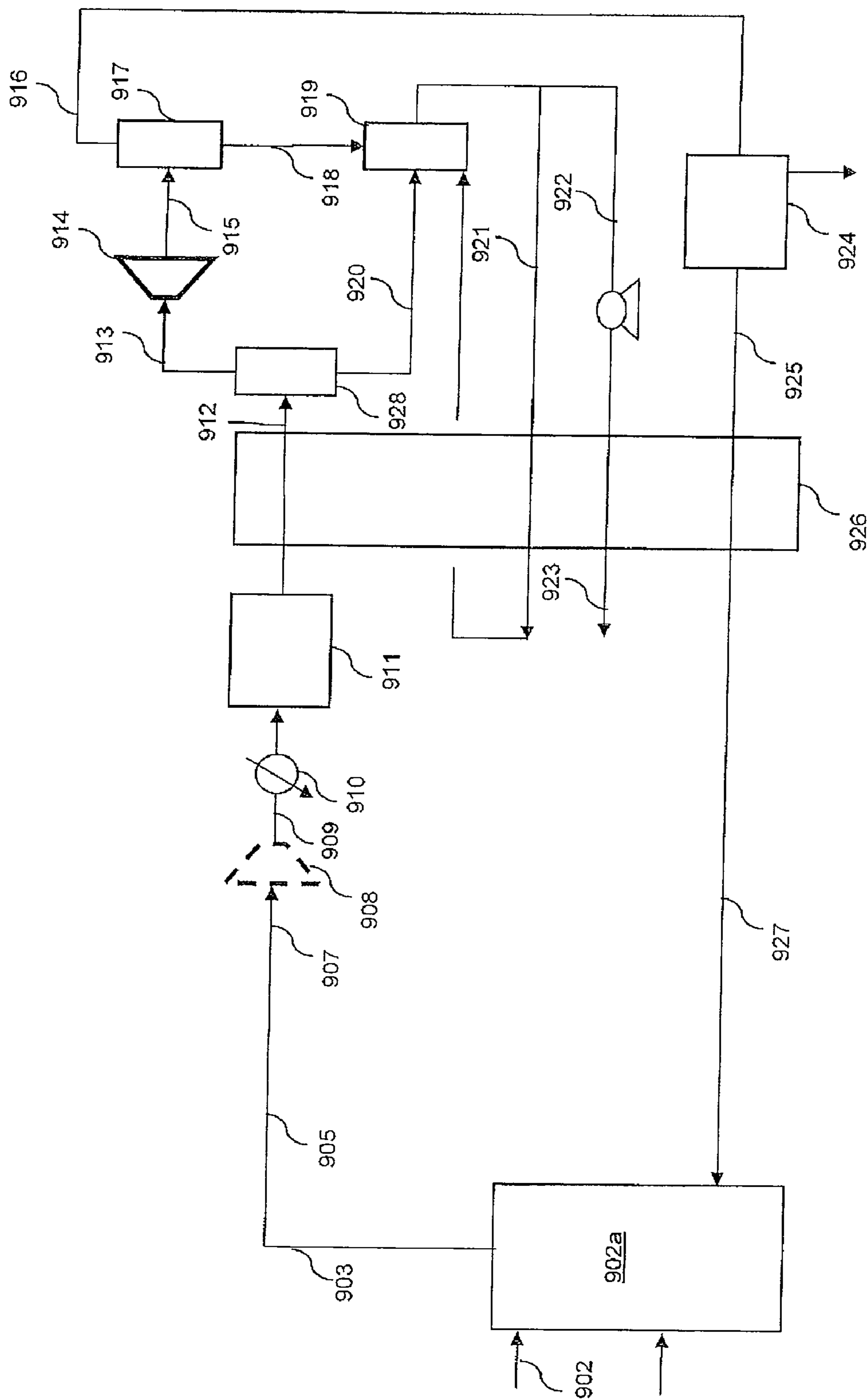


FIG. 12

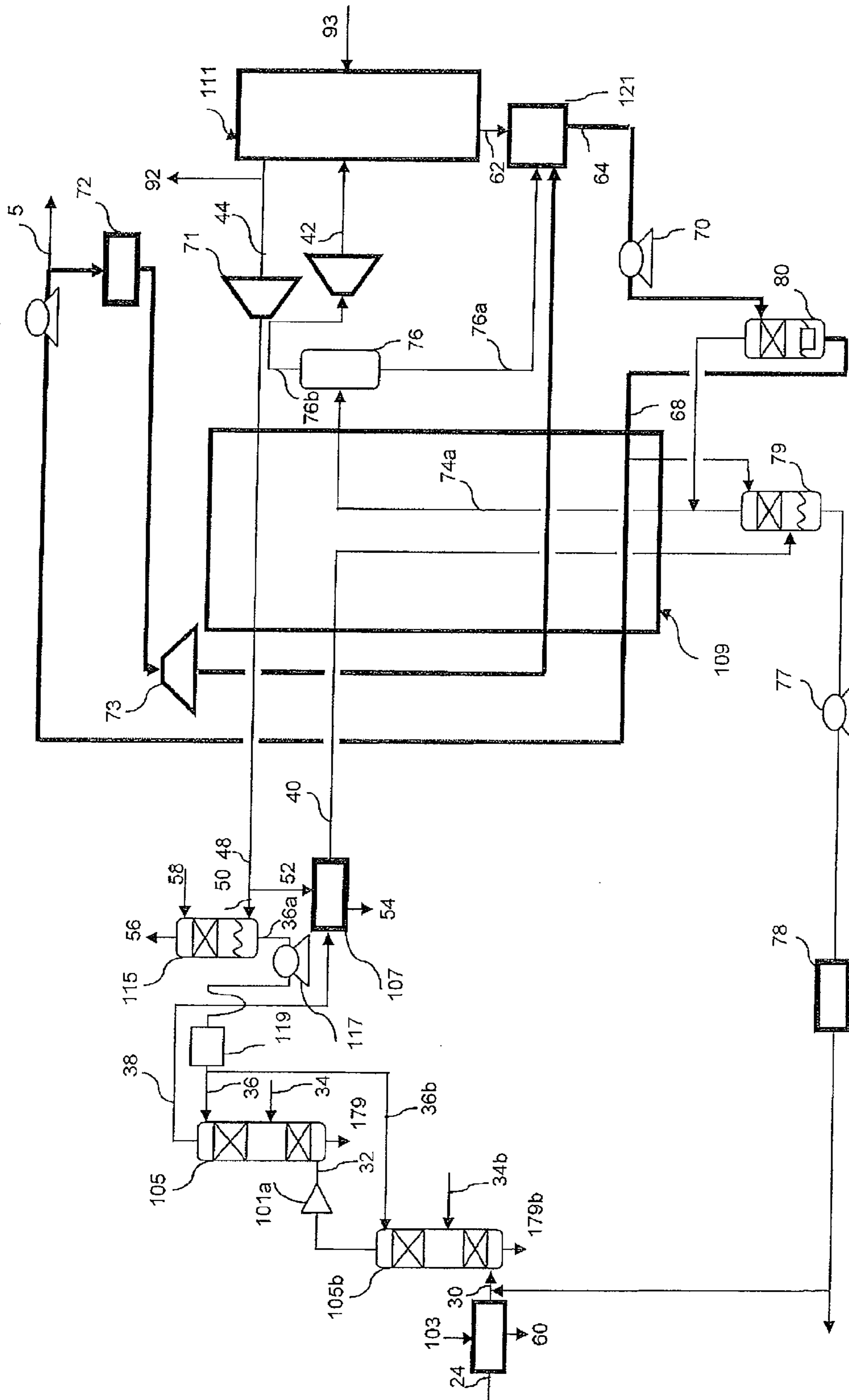


FIG. 13

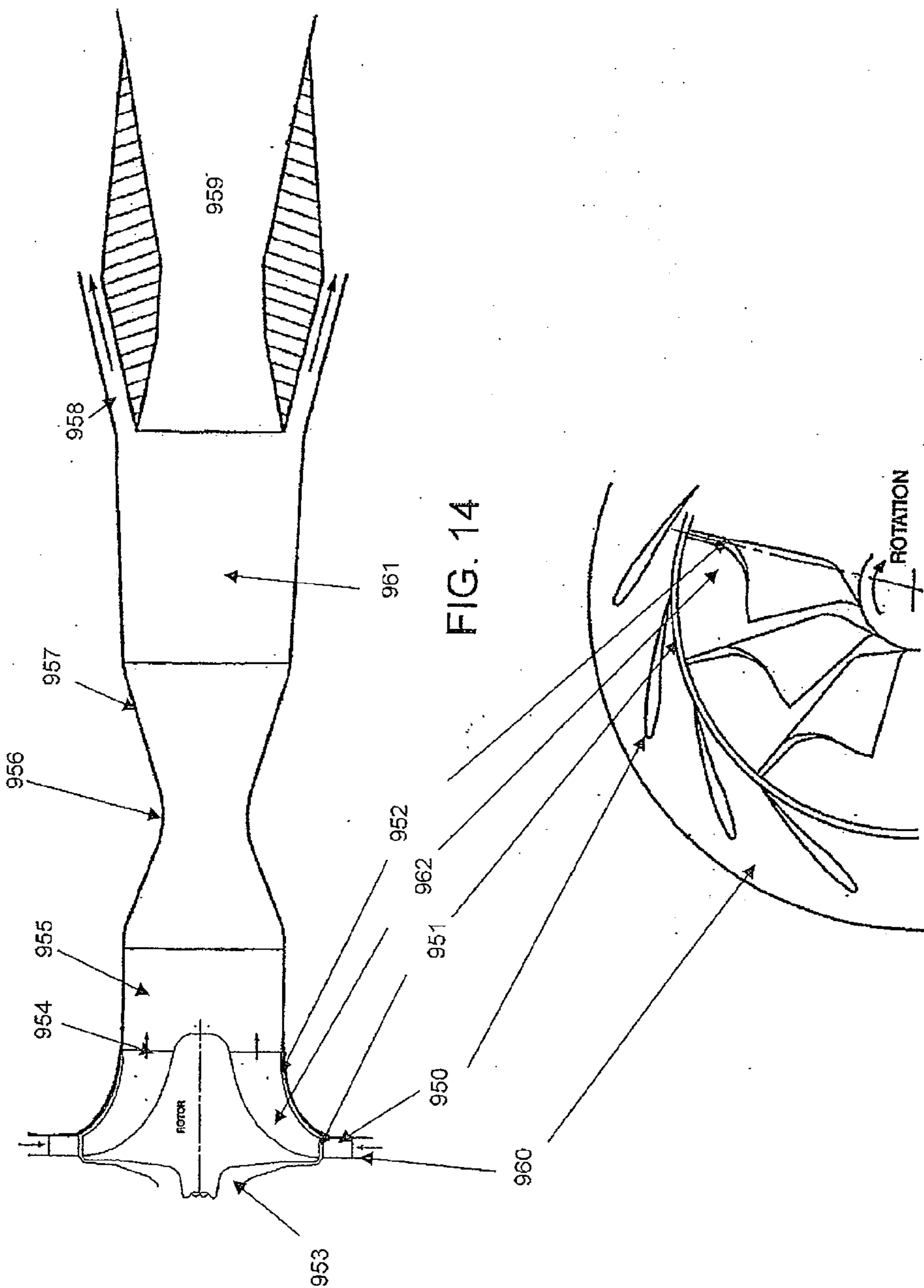


FIG. 14

FIG. 15

CO₂ RECOVERY METHOD USING CRYO-CONDENSATION

[0001] The present invention relates to a method of capturing carbon dioxide in a fluid comprising at least one compound more volatile than carbon dioxide CO₂, for example methane CH₄, oxygen O₂, argon Ar, nitrogen N₂, carbon monoxide CO, helium He and/or hydrogen H₂.

[0002] The invention can be notably applied to units producing electricity and/or steam from carbon fuels such as coal, hydrocarbons (natural gas, fuel oil, petrochemical residue, etc), household waste, biomass but can also be applied to gases from refineries, chemical plants, steel-making plants or cement works, to the treatment of natural gas as it leaves production wells. It could also be applied to the flue gases from boilers used to heat buildings or even to the exhaust gases from transport vehicles, and more generally to any industrial process that generates CO₂-containing flue gases.

[0003] Carbon dioxide is a greenhouse gas. For environmental and/or economic reasons, it is becoming increasingly desirable to reduce or even eliminate discharges of CO₂ into the atmosphere by capturing it and then, for example, storing it in appropriate geological layers or by realizing it as an asset in its own right.

[0004] A certain number of techniques for capturing carbon dioxide, for example methods based on scrubbing the fluids with solutions of compounds that separate the CO₂ by chemical reaction, for example scrubbing using MEA, are known. These methods typically have the following disadvantages:

[0005] high energy consumption (associated with the regeneration of the compound used to react with the CO₂),

[0006] degradation of the compound that reacts with the carbon dioxide,

[0007] corrosion due to the compound reacting with the carbon dioxide.

[0008] In the field of cryo-condensation, that is to say of cooling until solid CO₂ appears, mention may be made of document FR-A-2820052 which discloses a method allowing CO₂ to be extracted by anti-sublimation, that is to say by solidification from a gas without passing via the liquid state. The cold required is provided by means of fractionated distillation of refrigerating fluids. This method consumes a great deal of energy.

[0009] Document FR-A-2894838 discloses the same type of method, with some of the liquid CO₂ produced recirculated. The cold may be supplied by vaporizing LNG (liquefied natural gas). This synergy reduces the specific energy consumption of the method, although this remains high despite this, and requires an LNG terminal.

[0010] Document U.S. Pat. No. 3,614,872 describes a separation method in which the adiabatic and isentropic expansion of the carbon dioxide yields a refrigerating fluid.

[0011] It is one object of the present invention to provide an improved method of capturing carbon dioxide from a fluid containing CO₂ and at least one compound more volatile than the latter.

[0012] The invention relates first of all to a method for producing at least one CO₂-lean gas and one or more CO₂-rich primary fluids from a process fluid containing CO₂ and at least one compound more volatile than CO₂ and implementing:

[0013] a) a first cooling of said process fluid by exchange of heat with no change in state;

[0014] b) a second cooling of at least part of said process fluid cooled in step a) so as to obtain at least one solid containing predominantly CO₂ and at least said CO₂-lean gas; and

[0015] c) a step comprising liquefaction and/or sublimation of at least part of said solid and making it possible to obtain said one or more CO₂-rich primary fluids;

said method being characterized in that at least part of the cold required to perform said first cooling and/or said second cooling is supplied by one or more refrigerating cycles each comprising at least one near-isentropic expansion of a gas.

[0016] The process fluid generally comes from a boiler or any plant that produces flue gases. These flue gases may have undergone various pre-treatments, notably with a view to removing NO_x (oxides of nitrogen), dust, SO_x (oxides of sulfur) and/or water.

[0017] Prior to separation, the process fluid is either monophasic, in gaseous or liquid form, or polyphasic. What is meant by "gaseous" form is "essentially gaseous" form, that is to say that it may notably contain dust, solid particles such as soot and/or droplets of liquid.

[0018] The process fluid contains CO₂ that is to be separated from the other constituents of said fluid by cryo-condensation. These other constituents comprise one or more compounds more volatile than carbon dioxide in terms of condensation, for example methane CH₄, oxygen O₂, argon Ar, nitrogen N₂, carbon monoxide CO, helium He and/or hydrogen H₂. The process fluids generally comprise predominantly nitrogen or predominantly CO or predominantly hydrogen.

[0019] In step a) the process fluid is first of all cooled without a change in state. This cooling may advantageously take place at least in part by exchange of heat with CO₂-rich fluids from the separation process. In addition or as an alternative, it may advantageously take place at least in part by exchange of heat with the CO₂-lean gas from the separation process. These cold fluids from the separation process are heated up, while the process fluid is cooled down. This makes it possible to reduce the amount of energy required for the cooling operation.

[0020] Step b) consists in solidifying the initially gaseous CO₂ by raising the process fluid to a temperature below the triple point for CO₂ while the partial pressure of the CO₂ in the process fluid is below that of the triple point for CO₂. For example, the total pressure of the process fluid is close to atmospheric pressure. This solidification operation is sometimes known as "cryo-condensation" or "anti-sublimation" of the CO₂ and, by extension, of the process fluid.

[0021] According to one particular embodiment, all the components of the process fluid which do not solidify in step a) or which are not lumped together with the solid CO₂, remain in the gaseous state. These constitute the CO₂-lean gas.

[0022] Certain compounds more volatile than CO₂ do not solidify and remain in the gaseous state. Together with the non-solidified CO₂ these will constitute said CO₂-lean gas, that is to say will constitute said gas that comprises less than 50% CO₂ by volume and preferably less than 10% CO₂ by volume. According to one particular embodiment, said CO₂-lean gas contains less than 1% CO₂ by volume. According to another particular embodiment, it contains more than 2% thereof. According to another particular embodiment, it con-

tains more than 5% thereof. A solid comprising predominantly CO₂, that is to say containing at least 90% by volume if considered in the gaseous state, preferably containing at least 95% by volume, and more preferably still containing at least 99% CO₂ by volume, is formed.

[0023] This solid may comprise other compounds than CO₂. Mention may, for example, be made of other compounds which might also have solidified, or alternatively of bubbles and/or drops of fluid contained within said solid lump. This explains how the solid could potentially consist of not only solid CO₂. This “solid” may contain non-solid parts such as fluid inclusions (drops, bubbles, etc).

[0024] This solid is then isolated from the compounds that have not solidified after cryo-condensation and recovered. Next, in step c), it is returned to temperature and pressure conditions such that it changes into a fluid, liquid and/or gaseous, state. At least part of said solid may then liquefy. This then gives rise to one or more CO₂-rich primary fluids. These fluids are said to be “primary” to distinguish them from treatment fluids which are said to be “secondary”. What is meant by “CO₂-rich” is something “comprising predominantly CO₂” within the meaning defined hereinabove.

[0025] The inventors have demonstrated that it is particularly advantageous to carry out the first and/or the second cooling of the process fluid using one or more refrigerating cycles each comprising at least one near-isentropic expansion of a gas. These refrigerating cycles consist of several steps which cause a so-called “working” fluid to pass via several physical states characterized by given composition, temperature, pressure, etc conditions. The presence, among the steps of the cycle, of at least one near-isentropic expansion, that is to say of an expansion that causes the entropy of the expanded fluid to increase by less than 25%, preferably less than 15% and more preferably still, less than 10% makes it possible to improve the energy consumption of the separation process. By convention, entropy is considered to be zero at a temperature of zero K (kelvin).

Depending on circumstances, the method according to the invention may comprise one or more of the following features:

[0026] said refrigerating cycles each comprising at least one near-isentropic expansion employ working fluids chosen from the following:

[0027] an auxiliary fluid containing nitrogen and/or argon and/or a mixture of air gases;

[0028] a fluid comprising all or some of said CO₂-lean gas or derived from all or part of said CO₂-lean gas; and/or

[0029] a fluid comprising all or part of said process fluid or derived from all or part of said process fluid.

[0030] at least part of the cold required for performing said second cooling is supplied by exchange with:

[0031] the working fluid of one of said refrigerating cycles each comprising at least one near-isentropic expansion;

[0032] an auxiliary fluid containing nitrogen and/or argon and/or a mixture of air gases;

[0033] a fluid containing all or part of said CO₂-lean gas or derived from all or part of said CO₂-lean gas; and/or

[0034] a fluid containing all or part of said process fluid or derived from all or part of said process fluid.

[0035] at least part of the cold needed to carry out said second cooling is supplied by direct exchange.

[0036] at least one of said refrigerating cycles each comprising at least one near-isentropic expansion employs all or part of said process fluid as working fluid.

[0037] at least one of said refrigerating cycles each comprising at least one near-isentropic expansion comprises at least one near-isentropic expansion supplying external work.

[0038] the method further comprises a step d) of heating up at least one of said CO₂-rich primary fluids and/or said CO₂-lean gas by cold compression and/or by exchange of heat with an auxiliary fluid. This auxiliary fluid may be the process fluid.

[0039] said near-isentropic expansion of at least one of said refrigerating cycles each comprising at least one near-isentropic expansion comprises one or more of the following steps:

[0040] causing the process fluid to rotate about an axis substantially parallel to the direction of flow of said process fluid;

[0041] raising the speed of the process fluid;

[0042] separating the solid CO₂ from the process fluid using a centrifugal effect;

[0043] decelerating the gas that has become CO₂-lean.

[0044] in step b), at least part of said process fluid cooled in step a) is cooled in such a way as further to obtain a liquid comprising predominantly CO₂.

[0045] said process fluid comes from industrial flue gases.

[0046] said process fluid comes from a steel-making plant.

[0047] said process fluid comes at least partially from a blast furnace.

[0048] said CO₂-lean gas is at least partially recirculated into said blast furnace.

[0049] said process fluid comes at least partially from a refinery and/or from a chemical plant.

[0050] said process fluid comes at least partially from the gasification and/or the partial oxidation and/or an oxygen reforming of a given carbon fuel.

[0051] said process fluid comes from a plant comprising an air separation unit.

[0052] said near-isentropic expansion of at least one of said refrigerating cycles each comprising at least one near-isentropic expansion of a gas is carried out in said air separation unit.

[0053] some of the cold required to carry out said first cooling and/or said second cooling is supplied by at least one refrigerating cycle comprising an expansion of a fluid that is not a near-isentropic expansion.

[0054] said at least one near-isentropic expansion providing external work provides work that is at least partially used to compress a fluid of said production method.

[0055] To provide another part of the cold required to carry out the first and/or second coolings, recourse may be had to one or more cycles comprising an expansion of a fluid that is not a near-isentropic expansion, for example reverse-Rankine cycles. These cycles are said to be reversed because they are used as refrigerating cycles. Their benefit, as a supplement to the refrigerating cycles employing near-isentropic expansion, is that they do not require a large amount of working fluid. By contrast, they are less energy-efficient.

[0056] According to one embodiment, some of the near-isentropic expansions of the refrigerating cycle or cycles provide work. They are, for example, carried out by introducing working fluid into a turbine.

[0057] The working fluids may be of varying kinds. According to various embodiments, these fluids may comprise nitrogen and/or argon. They may also comprise all or part of the CO₂-lean gas obtained or of the process fluid. These fluids may be mixed with other fluids or have undergone intermediate steps of compression, expansion, etc.

[0058] When the working fluid of the refrigerating cycle comprises all or part of the process fluid, the near-isentropic expansion or expansions that do not provide external work may give rise to a cooling of the working fluid such that solid CO₂ appears. This may constitute all or part of the second cooling of the process fluid. According to one particular embodiment, these near-isentropic expansions are carried out through a Venturi (a throat with Venturi effect).

[0059] The abovementioned causing of the fluid to rotate can be obtained by any conventional means, for example by suitably oriented vanes. The increase in speed is achieved through a Venturi effect. The temperature of the working fluid drops. Solid particles of CO₂ appear. The fluid has a rotational movement about an axis substantially parallel to the direction of the flow, like a corkscrew. This creates a centrifugal effect allowing these solid particles to be recovered at the periphery of the flow.

[0060] According to a preferred embodiment, any work that might be produced by the near-isentropic expansion or expansions serves in part to compress the fluids in other steps of the method.

[0061] The invention also relates to the method applied to industrial flue gases with a view to capturing CO₂.

[0062] According to one particular embodiment, these flue gases come from a plant producing energy (steam, electricity) and may have undergone pretreatments.

[0063] Other specifics and advantages will become apparent from reading the following description given with reference to the figures in which:

[0064] FIG. 1 schematically depicts a plant employing a method for purifying CO₂ according to the invention, with a refrigerating cycle employing an auxiliary fluid as working fluid,

[0065] FIG. 2 schematically depicts part of a plant employing an alternative form of this method, with a refrigerating cycle using the CO₂-lean gas by way of working fluid and comprising a near-isentropic expansion with the production of work,

[0066] FIG. 3 schematically depicts part of a plant employing another alternative form of this method, with a refrigerating cycle using the CO₂-lean gas as working fluid and comprising a near-isentropic expansion with the production of work,

[0067] FIG. 4 schematically depicts part of a plant employing an alternative form of the method with a refrigerating cycle using the process fluid as working fluid and comprising a near-isentropic expansion with the production of work, during which there is no cryo-condensation of CO₂,

[0068] FIG. 5 schematically depicts part of a plant employing an alternative form of the method with a refrigerating cycle using the process fluid as working fluid and comprising a near-isentropic expansion with the production of work, during which there is cryo-condensation of CO₂,

[0069] FIG. 6 schematically depicts part of a plant employing an alternative form of the method with a refrigerating cycle using the process fluid as working fluid and comprising a near-isentropic expansion without the production of work, during which there is cryo-condensation of CO₂,

[0070] FIG. 7 schematically depicts part of a plant employing an alternative form of the method, in which the second cooling also comprises liquefaction and further comprising a refrigerating cycle using the process fluid as working fluid and comprising near-isentropic expansions without the production of work during which expansions there is cryo-condensation of CO₂.

[0071] FIG. 8 schematically depicts the use of a method according to the invention in a plant for producing electricity on the basis of coal with combustion in air.

[0072] FIG. 9 schematically depicts the use of a method according to the invention in a plant for producing electricity on the basis of coal with hybrid combustion or combustion in oxygen.

[0073] FIG. 10 schematically depicts the use of a method according to the invention in a steel-making plant.

[0074] FIG. 11 schematically depicts the use of a method according to the invention in a plant for producing synthesis gas operating on oxygen.

[0075] FIG. 12 schematically depicts the use of a method according to the invention in a plant for producing carbon monoxide from a synthesis gas that comes from a steam reforming of a synthesis gas.

[0076] FIG. 13 schematically depicts the use of a method according to the invention with, on the one hand, a cycle for producing energy using the cold of fusion of solid CO₂ and, on the other hand, additional purifications by distillation of the compounds less volatile than CO₂, then the compounds more volatile than CO₂.

[0077] FIGS. 14 and 15 depict a turbine for carrying out a near-isentropic expansion of the process fluid with the production of external work in accordance with the invention.

[0078] The plant illustrated in FIG. 1 implements the steps described below.

[0079] The fluid 24 consisting of flue gases is compressed in a compressor 101, notably to compensate for the pressure losses in the various pieces of equipment in the plant. Let us note that this compression may also be combined with the compression known as the draft compression of the boiler that produces the flue gases. It may also be carried out between other steps of the method, or downstream of the CO₂ separation method;

[0080] The compressed fluid 30 is injected into a filter 103 to eliminate particles down to a level of concentration of below 1 mg/m³, preferably of below 100 µg/m³.

[0081] Next, the dust-free fluid 32 is cooled to a temperature close to 0° C., generally of between 0° C. and 1020 C., so as to condense the water vapor it contains. This cooling is carried out in a tower 105, with water injected at two levels, the cold water 36 and water 34 at a temperature close to ambient temperature. It is also possible to conceive of indirect contact. The tower 105 may or may not have packings.

[0082] The fluid 38 is sent to a unit that eliminates residual water vapor 107, for example using one and/or another of the following methods:

[0083] Adsorption on fixed beds, fluidized beds and/or rotary dryer, the adsorbent potentially being activated alumina, silica gel or a molecular sieve (3A, 4A, 5A, 13X, . . .);

- [0084] Condensation in a direct-contact or indirect-contact exchanger.
- [0085] The dried fluid **40** is then introduced into the exchanger **109** where the fluid is cooled down to a temperature close to, but in all events higher than, the temperature at which CO₂ solidifies. This temperature can be determined by a person skilled in the art aware of the pressure and composition of the process fluid **40**. This temperature is situated at around about -100°C . if the CO₂ content of the process fluid is of the order of 15% by volume and for a pressure close to atmospheric pressure.
- [0086] The fluid **42** which has undergone a first cooling **109** is then introduced into a vessel **111** where it continues to be cooled down to the temperature that provides the desired level of CO₂ capture. Cryo-condensation of at least part of the CO₂ contained in the fluid **42** occurs producing, on the one hand, a CO₂-lean gas **44** and, on the other hand, a solid **62** comprising predominantly CO₂. The gas **44** leaves the vessel **111** at a temperature of the order of -120°C . This temperature is chosen as a function of the target level of CO₂ capture. At this temperature, the CO₂ content of the gas **44** is of the order of 1.5% by volume, namely a capture level of 90% starting out from a process fluid containing 15% CO₂. There are various technologies that can be used for this vessel **111**:
- [0087] Continuous solid cryo-condensation exchanger in which solid CO₂ is produced in the form of carbon dioxide snow, is extracted, for example, using a screw and pressurized to introduce it into a bath of liquid CO₂ **121** in which a pressure higher than the triple point pressure for CO₂ obtains. This pressurization can also be carried out batchwise in a system of silos. Continuous solid cryo-condensation may itself be performed in various ways:
- [0088] Scraped surface exchanger, the scrapers for example being in the form of screws to encourage extraction of the solid;
- [0089] Fluidized bed exchanger so as to carry the carbon dioxide snow along and clean out the tubes using particles for example of a density greater than that of the carbon dioxide snow;
- [0090] Exchanger in which solid is extracted by vibration, ultrasound, a pneumatic or thermal effect (intermittent heating so as to cause the carbon dioxide snow to fall);
- [0091] Accumulation on a smooth surface with periodic "natural" fall into a tank;
- [0092] Batchwise solid cryo-condensation: in this case, several exchangers in parallel can be used alternately. They are then isolated, pressurized to a pressure higher than the triple point pressure for CO₂, so as to liquefy the solid CO₂ and possibly partially vaporize it.
- [0093] The fluid **46** is then heated up in the exchanger **109**. As it leaves, the fluid **48** can also be used notably to regenerate the unit used for eliminating residual vapor **107** and/or for producing cold water **36** by evaporation in a direct-contact tower **115** into which a dry fluid **50** is introduced which then becomes saturated with water, vaporizing some of it. The cold water could then potentially undergo additional cooling in a refrigerator unit **119**.
- [0094] The solid **62** comprising predominantly CO₂ is transferred to a bath **121** of liquid CO₂.

[0095] This bath **121** needs to be heated in order to remain liquid, to compensate for the addition of cold from the solid **62** (latent heat of fusion and sensible heat). This can be done in various ways:

[0096] by exchange of heat with a hotter fluid **72**. The cold energy from the fluid **74** can be used elsewhere in the method,

[0097] by direct exchange, for example by tapping a fluid **80** from the bath **121**, heating it in the exchanger **109**, and reinjecting it back into the bath **121**.

[0098] Liquid **64** comprising predominantly CO₂ is tapped from the bath **121**. This liquid is split into three streams. In the example, the first is obtained by an expansion **65** to 5.5 bar absolute producing a diphasic, gas-liquid, fluid **66**. The second, **68**, is obtained by compression **67**, for example to 10 bar. The third, **70**, is compressed for example to 55 bar. The 5.5 bar level provides cold at a temperature close to the triple point temperature for CO₂. The 10 bar level allows the transfer of the latent heat of vaporization of the fluid **68** at around -40°C . Finally, at 55 bar, the fluid **70** does not vaporize during the exchange **109**. There is efficient use to be made of the cold energy contained in the fluid **64** during the exchange **109** while at the same time limiting the amount of energy required to produce a purified and compressed stream **5** of CO₂.

[0099] Part of the cold required for the first cooling **109** and for the second cooling **111** is provided by a refrigerating cycle **200** employing a working fluid **51** which is argon. It comprises, in succession: a compression **129**, possibly two compressions **56** and **57**, a cooling by indirect exchange **109**, a near-isentropic expansion **131** which gives rise to cooling, a heating-up in the vessel **111**, and a heating-up **109**. During the cooling **109**, part of the working fluid is tapped off then undergoes near-isentropic expansion **130**, followed by indirect exchange **109** and finally compression **128** before reaching the compression stage **129**. The near-isentropic expansions **130** and **131** supply work part of which can be used for the compressions **56** and **57**.

[0100] This cycle **200** produces cold at between about -100 and -120°C . for the cryo-condensation **111** and between about 5°C . and -100°C . in order to offset the deficit of cold during the exchange **109**.

[0101] Another part of the cold needed for the first cooling **109** is provided by an additional refrigerating cycle **181**, **183**, for example of the reverse Rankine type.

[0102] Another part of the cold needed for the second cooling **111** is provided by an additional refrigerating cycle **191**, **193**, for example of the reverse Rankine type.

[0103] Following the indirect exchange **109**, the CO₂-rich primary fluids **66**, **68**, **70** are compressed in stages **141**, **142**, **143**. For example, the first stages compress gaseous streams. If need be, the compressed CO₂ **75** is cooled by an indirect-contact exchanger to convert it to liquid form. It is then mixed with the stream **73**. This liquid mixture is pumped to the transport pressure (fluid **5**). As the transport pressure is generally supercritical, the supercritical fluids will, by extension, be considered to be liquid at a temperature below that of the critical point for CO₂.

[0104] FIGS. 2 to 7, which depict examples according to particular embodiments of the invention, do not depict the steps which apply to the process fluid **40** prior to its first cooling **109**, nor do they depict the compression of the CO₂-rich primary fluids after the exchange of heat **109**. They depict

only changes by comparison with FIG. 1 relating essentially to the refrigerating cycles that provide the cold for the exchanges 109 and 111.

[0105] FIG. 2 illustrates an alternative form of the near-isentropic expansion with production of work, in which the working fluid is the CO₂-lean gas 44. The cryo-condensation method is the same as in FIG. 1. Only the changes are detailed below.

[0106] The CO₂-lean gas 44 is compressed, for example by a multi-stage compressor 315. On leaving, the fluid 303 is cooled if necessary to the inlet temperature for the exchanger 109 by the exchanger 316. This may be a direct-contact or an indirect-contact exchanger.

[0107] The compressed CO₂-lean gas 304 is cooled in the exchanger 109 so that it can be expanded in the turbine 312 (near-isentropic expansion) so as to provide some of the cold needed for the exchange 111. The fluid 307 leaving the exchanger 111 is once again expanded (near-isentropic expansion) to provide work and cold for the exchanger 111 via the fluid 308. This loop in which the CO₂-lean gas is expanded can be repeated as many times as necessary.

[0108] After the exchanger 111, the CO₂-lean gas 46 is heated up in the exchanger 109. The outgoing fluid 48 is processed like the fluid 48 in FIG. 1.

[0109] Some of the cold needed for the exchanger 111 may be supplied by a refrigerating cycle 191, 193 of the Rankine type.

[0110] FIG. 3 illustrates another alternative form of the near-isentropic expansion with the production of work.

[0111] The CO₂-lean gas 44 gives up cold energy in the exchangers 111 and 109. It is then compressed by the multi-stage compressor 415. Next, it is cooled if necessary to the inlet temperature of the exchanger 109 in the exchanger 416. This may be a direct-contact or an indirect-contact exchanger.

[0112] The CO₂-lean gas 404 is once again cooled in the exchanger 109 before it is being expanded by the turbine 412. This near-isentropic turbine produces the cold required to compensate for part of the deficit of cold energy in the exchanger 111.

[0113] Next, the fluid 407 is expanded again by the near-isentropic turbine 414. The fluid 408 gives up its cold energy to compensate for part of the deficit of cold energy in the exchanger 111. This loop in which the CO₂-lean gas is expanded can be repeated as many times as necessary.

[0114] Following the exchanger 111, the CO₂-lean gas 46 is heated up in the exchanger 109. Finally, the outgoing fluid 48 is processed as the fluid 48 in FIG. 1.

[0115] FIG. 4 illustrates another alternative form of the near-isentropic expansion with production of work.

[0116] The process fluid 40 is compressed by the compressor 512 which may be a multi-stage compressor. The CO₂-lean gas is expanded in a near-isentropic turbine 514. The temperature of the fluid 503 must remain above the cryo-condensation temperature for CO₂.

[0117] Part of the CO₂ contained in the fluid 503 then condenses in the vessel 111. The solid CO₂ 62 is tipped into the liquid bath 121 and the next steps are the same as those described in FIG. 1 (from the bath 121 and stream 64 onwards). The CO₂-lean gas 44 passes its cold energy to the exchangers 111 and 109. The outgoing fluid 48 is processed like the fluid 48 of FIG. 1.

[0118] FIG. 5 illustrates another alternative form of the near-isentropic expansion with the production of work, in which the working fluid is the process fluid.

[0119] A near-isentropic expansion with production of work is carried out on the fluid 42 in the turbine 612 so as to cool the fluid to a temperature below the cryo-condensation temperature for CO₂ and thus produce solid CO₂ in the form of carbon dioxide snow together with a CO₂-lean gas 602.

[0120] This expansion turbine 612 needs to be designed with a great deal of care. It has to be suited to the high flow rates such as those of the flue gases 40 of an industrial plant, have very good isentropic efficiency, and be resistant to potential additional erosion due to the presence of solid CO₂. To achieve this, carbon dioxide snow is allowed to be present in the rotor part of the turbine (the region contained between the leading edge 951 and the trailing edge 954 in FIGS. 14 and 15) and is forbidden or minimized in the stator part 960 upstream of the rotor part (the region contained upstream of the trailing edge of the stator vanes 950) in order notably not to cause erosion of the leading edge of the vanes 952 of the rotor part. Put differently, it is preferable for the CO₂ to be in the vapor or supersaturated vapor state in the stator part or for it to have carbon dioxide snow nuclei that are small enough (less than 10 μm, preferably 1 μm hydraulic diameter) to avoid eroding the rotor part.

[0121] The turbine may be a radial turbine (centripetal or centrifugal). It may be a supersonic shockwave turbine. It may be axial.

[0122] The latter technology is the best suited to high flow rates, but does require numerous successive stator and rotor stages. To avoid erosion, it will be preferable for the carbon dioxide snow to be separated out downstream of each rotor stage before the fluid enters the next stator stage. The first two technologies have the advantage of remaining effective for high expansion ratios (in excess of 10) thus making it possible to avoid having to perform numerous separation operations.

[0123] Moreover, other precautions have preferably to be taken in order to create such a turbine:

[0124] heterogeneous nucleation (on the stator and rotor surfaces) needs to be minimized, for example by heating some of these surfaces or by applying special coatings;

[0125] nucleation needs to be delayed by eliminating compounds less volatile than CO₂ (including solid particles) before they enter the turbine, so that they do not form nuclei encouraging the nucleation of solid CO₂;

[0126] the erosion resistance of the surfaces needs to be increased by using stronger metals such as titanium or by using special coatings or surface treatments;

[0127] in the case of centripetal radial turbines, it is preferable for a sweeping gas to be passed across the back of the impeller 953. This gas mixes with the expanded gas at the interface between the stator part (vanes) and the rotor part (impeller) and thus avoids the formation and build-up of solids behind the impeller.

[0128] This carbon dioxide snow is then separated from the CO₂-lean gas in a separator 612 to obtain a solid comprising predominantly CO₂ 62 and a CO₂-lean gas 44.

[0129] This separation may be performed downstream of the rotor part by causing the fluid in the rotor part to rotate and by using the centrifugal effect to separate a CO₂-rich fraction at the periphery from a CO₂-lean fraction at the center. It may also be advantageous to increase the speed and therefore achieve an additional expansion of the fluid in a convergent nozzle 956 (a turbine known as a Laval turbine). By reducing the pressure before decelerating the gas the amount of solidified CO₂ can be increased. Most of the CO₂-lean gas is

recovered at the center of the flow **959** and most of the solid CO₂ is recovered at the periphery **958**, mixed in with a fraction of the gas.

[0130] The benefit of a turbine for performing solid cryo-condensation is that a great deal of solid CO₂ can be generated in a very small volume as compared with indirect-exchange systems.

[0131] If necessary, an additional refrigerating cycle **191**, **193** of the Rankine type or which includes a near-isentropic expansion of a working fluid with or without the production of work provides the separator **612** with cold energy. The solid **62** comprising predominantly CO₂ is tipped into the liquid bath **121** and the next steps are the same as those depicted in FIG. 1.

[0132] The CO₂-lean gas **44** is heated up by exchange of heat with the process fluid in the exchanger **109**. The fluid **605** is then compressed to a pressure higher than or equal to atmospheric pressure. Finally, the outgoing fluid **48** is processed as in FIG. 1.

[0133] FIG. 6 illustrates one embodiment with near-isentropic expansion without the production of work.

[0134] The process fluid **42** is still cooled to below the cryo-condensation temperature for CO₂ in the vessel **111** to produce a cooled CO₂-lean gas **701**. It is also possible for this vessel to be situated after the “expansion/Venturi” part **702** of the method, and will now be described.

[0135] Some of the CO₂ to be captured solidifies in the form of a solid containing predominantly CO₂ **62** and is extracted from the vessel **111**. To improve CO₂ capture, the fluid **701** is made to rotate about an axis that is substantially parallel to the direction in which it flows using a system of fixed vanes **717**.

[0136] The fluid **703** is expanded as it leaves the vanes and cools, to below the cryo-condensation temperature for CO₂, without producing work. The expansion may take place through the Venturi effect by passing the fluid through a restriction **718**. Solid particles comprising predominantly CO₂ form and are recovered at the periphery of the flow thanks to the centrifugal effect caused by the rotation of the fluid.

[0137] A mixture **705** of solid comprising predominantly CO₂ and gas is recovered. The outgoing non-condensables **44**, **46** give up their cold energy in the exchangers **111** and **109**.

[0138] The stream **705** is made up predominantly of solid, although it may be necessary to separate the residual gas from the solid in a separator **731**. The non-condensable part then gives up its cold energy in the exchangers **111** and **109**.

[0139] The solid comprising predominantly CO₂ **62** is tipped into the liquid bath **121** and undergoes the same steps as those described in FIG. 1.

[0140] The streams **48** are used to cool the water, in the same way as the stream **50** in FIG. 1.

[0141] FIG. 7 illustrates another embodiment with near-isentropic expansion without the production of work.

[0142] The process fluid **40** is under pressure, for example as much as 60 bar (compression performed by the compressor **101** or by an additional compressor). It may potentially be more concentrated in CO₂ than in the other examples, typically containing between 50 and 90% by volume.

[0143] The exchange **809** comprises the same features as the exchange **109** in FIG. 1. The exchanger **811** cools the process fluid **42** to a temperature below the liquefaction tem-

perature of CO₂. From this there emerges a cooled process fluid **801** which is sent to a separator **812**.

[0144] A CO₂-rich liquid **816** is extracted by the separator **812**. The residual fluid **802** is made to rotate about an axis substantially parallel to the direction in which it flows by a system of fixed vanes **817**. It is expanded as it leaves **803** the vanes having been rotated and cooled to below the cryo-condensation temperature for CO₂ without producing work. The expansion may take place through a Venturi effect by passing the fluid through a restriction **818**.

[0145] Solid particles comprising predominantly CO₂ form and are recovered at the periphery of the flow thanks to the centrifugal effect caused by the rotating of the fluid. The stream **805** is made up predominantly of solid, although it may be necessary to separate the residual gas from the solid in a separator **841**. The non-condensables **44** give up their cold energy in the exchangers **811** and **809**.

[0146] In order to improve the level of CO₂ capture, a second (or even a third or more) step in which the fluid **806** undergoes a near-isentropic expansion with Venturi effect may be added. This step is identical to the previous one:

[0147] the fluid **806** is made to rotate about an axis substantially parallel to the direction in which it flows using a system of fixed vanes **807**;

[0148] after it has been made to rotate, the fluid leaving the vanes **808** is expanded to cool it to below the cryo-condensation temperature for CO₂ without the production of work. The expansion may take place through a Venturi effect by passing the fluid through a restriction **822**.

[0149] The solid **62** comprising predominantly CO₂ recovered at the outlet from the separators **841** and possibly **851** is tipped into the liquid bath **121** and processed as in FIG. 1. Streams **48** are used to cool the water, in the same way as the stream **50** in FIG. 1.

[0150] FIG. 8 depicts a plant for producing the electricity from coal, employing various units **4**, **5**, **6** and **7** for purifying the flue gases **19**.

[0151] A primary airflow **15** passes through the unit **3** in which the coal **15** is pulverized and carried along toward the burners of the boiler **1**. A secondary airflow **16** is applied directly to the burners in order to provide additional oxygen needed for near-complete combustion of the coal. Feed water **17** is sent to the boiler **1** to produce steam **18** which is expanded in a turbine **8**.

[0152] The flue gases **19** resulting from the combustion, comprising nitrogen, CO₂, water vapor and other impurities, undergo various treatments to remove some of said impurities. The unit **4** removes the NO_x for example by catalysis in the presence of ammonia. The unit **5** removes dust, for example using an electrostatic filter, and the unit **6** is a desulfurization system for removing the SO₂ and/or SO₃. The units **4** and **6** may be superfluous depending on the composition of the product required. The purified flow **24** from the unit **6** (or **5** if **6** is not present) is then sent to a low-temperature cryo-condensation purification unit **7** to produce a relatively pure flow **26** of CO₂ and a nitrogen-enriched residual flow **25**. This unit **7** is also known as a CO₂ capture unit and implements the method that forms the subject of the invention, as illustrated, for example in FIGS. 1 to 7.

[0153] FIG. 9 depicts a plant for producing electricity from coal, implementing various units **5** and **7** for purifying the flue gases **19**.

[0154] A primary airflow **15** passes through the unit **3** where the coal **15** is pulverized and carried along toward the

burners of the boiler 1. A secondary flow of oxidant 16 is supplied directly to the burners in order to provide the additional oxygen needed for near-complete combustion of the coal. This secondary oxidant is the result of the mixing of flue gases 94 recirculated using a blower 91 with oxygen 90 produced by a unit 10 for separating air gases. Feed water 17 is sent to the boiler 1 to produce steam 18 which is expanded in a turbine 8.

[0155] The flue gases 19 from the combustion of the coal, comprising nitrogen, CO₂, water vapor and other impurities, undergo various treatments to remove some of said impurities. The unit 5 (ESP) removes the dust, for example using an electrostatic filter. The dust-free flow 24 from the unit 5 is sent to a low-temperature cryo-condensation purification unit 7 to produce a relatively pure flow 26 of CO₂ and a nitrogen-enriched residual flow 25. This unit 7 is also known as a CO₂ capture unit and implements the method that forms the subject of the invention, as illustrated, for example, in FIGS. 1 to 7.

[0156] In this case, the presence of a unit for separating the air gases is used to provide cold at low level for the solid cryo-condensation of CO₂ in the unit 7 and to carry out cryo-condensation, preferably by direct exchange with the process gas. The fluid 93 may be in liquid, gaseous or diphasic form and consists of a mixture of cooled air gases. For example, this may be cold gaseous nitrogen or air (at between -56° C. and -196° C.), or alternatively liquid nitrogen or air. It is intended to be introduced into the vessel referenced 111 in FIGS. 1 to 4 and in FIG. 6, referenced 612 in FIG. 5, 731 in FIGS. 6, and 841, 851 in FIG. 7.

[0157] The unit 7 may also produce a fluid 92 which will be used in the unit for separating air gases. This may, for example, be a fraction of the lean gas leaving the vessel 111 in FIGS. 1 to 4 and 6, 612 in FIG. 5, 731 in FIGS. 7 and 841, 851 in FIG. 8. This lean gas in some way restores cold to the unit 10 at a temperature level higher than that afforded from the unit 10 by the fluid 93. It is advantageous for the flow rate of this injection of fluid 93 to be varied over time. For example, liquid nitrogen may be produced and stored by night, when energy is available and inexpensive and the liquid nitrogen may then be injected by day in order to reduce the energy consumption. The time at which the cold is produced by the unit 10 (for example liquid nitrogen) is separated from the time at which it is used in the unit 7. In such a circumstance, the near-isentropic expansion of a gas can be carried out in the unit 10 rather than in the unit 7.

[0158] This scheme may prove well suited to instances where existing plants are being modified, where replacing the primary air sent to the coal pulverizers with a mixture of recirculated flue gases plus oxygen could prove complicated, partly because of the increase in water content, the flue gases containing far more water than damp air, and partly for safety reasons, although that should not be overestimated.

[0159] Moreover, it may prove advantageous to combine the units 7 and 10 into a single unit, notably by carrying out one (or more) exchange(s) of heat between fluids of the 2 units.

[0160] FIG. 10 schematically depicts the use of a method according to the invention in a steel-making plant. A unit 10 for separating the air gases supplies oxygen 90 to a blast furnace 900 into which iron ore 901 and carbon products 902 (coal and coke) are also introduced. The blast furnace in that instance operates in the presence of little nitrogen.

[0161] The blast furnace gases 903 made up for example of 47% CO, 36% CO₂, 8% N₂ and 9% other compounds such as H₂ and H₂O can be split into two. Most 905 goes to the CO₂ capture unit with another proportion 904 used to reduce the nitrogen concentration in the loop. The fluid 905 is cooled beforehand in a direct-contact exchanger 906, has its dust removed in the filter 103, and is then compressed by a compressor 901, is cooled in an exchanger 105 and dried in a drier 107 before entering the low-temperature exchanger 109 where it will be cooled and then partially liquefied to a temperature close to the triple point for CO₂ without the formation of solid. The diphasic gas-liquid fluid 912 obtained is separated into a gaseous fraction 502 and a liquid fraction 920 in the separator 928. The gaseous fraction 502 is then cooled by near-isentropic expansion, for example in a turbine 514, so as to obtain a diphasic gas-solid fluid 503. This is separated in the vessel 111 into a gaseous fraction 44 and a CO₂-rich solid fraction 62. The solid fraction 62 is compressed, for example by an endless screw and mixed with the liquid 920 in the bath 121, which is heated by gas 72 produced by vaporizing liquid 74 in the exchanger 109. The liquid CO₂ 64 is compressed by a pump 69 to obtain a pressurized liquid 70 and is heated up in the exchanger 109 without undergoing vaporization or pseudo-vaporization if the pressure is above the supercritical pressure. The lean gas is successively heated up by a compressor 315 and by the exchanger 109.

[0162] The invention may also be adapted to types of blast furnace operating on enriched air, for example by adding a CO/N₂ separation using cryogenic distillation, cooling the gas 44 to the required temperature.

[0163] FIG. 11 schematically depicts the use of a method according to the invention in a plant for producing synthesis gas from an oxygen process (partial oxidation, gasification, auto-thermal reformer, etc.). A unit 10 for separating air gases supplies oxygen 90 to a reactor 900 into which a carbon product 902 (coal, natural gas, biomass, household waste, etc.) is introduced.

[0164] The synthesis gases 903 chiefly comprise the compounds CO, CO₂, H₂ and H₂O. The CO can be converted (in a so-called shift reaction) into CO₂ and H₂ in the presence of water vapor: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. The fluid 905 may possibly have its dust removed in a filter 103, then be compressed by a compressor 101, cooled in an exchanger 105 and dried in a dryer 107 before entering the low-temperature exchanger 109 where it may be partially liquefied at a temperature close to that of the triple point for CO₂. This diphasic gas-liquid fluid 912 is separated into a gaseous fraction 502 and a liquid fraction 920 in the separator 928. The gaseous fraction 502 is then cooled by near-isentropic expansion, for example in a turbine 514, to obtain a diphasic gas-solid stream 503. This is separated into a gaseous fraction 44 and a CO₂-rich solid fraction 62 in the vessel 111. The solid fraction 62 is mixed with the liquid 920 in the bath 121, which is heated with gas 74 produced by the vaporizing of the liquid 72 in the exchanger 109. The liquid CO₂ 64 is compressed by a pump and heated up in the exchanger 109 without vaporizing, or pseudo-vaporizing if the pressure is above the supercritical pressure. The lean gas 44 is successively heated up via a compressor 924 and the exchanger 109. This lean gas essentially consisting of hydrogen may be sent to a gas turbine to be combusted without the emission of CO₂. The unit 10 may supply hot nitrogen 90a which is introduced downstream of the dryers 910, and/or cold nitrogen 90b, introduced directly into the vessel 111 to increase the amount of CO₂ captured. In

the first instance, the expansion in the turbine **514** of the hot nitrogen present in the stream **502** provides additional cold energy for solid cryo-condensation of CO₂ in the turbine **514**; in the second instance, the cold nitrogen **90b**, by heating up upon contact with the fluid **503**, leads to solid cryo-condensation of the CO₂. The other benefit of hot nitrogen **90a** is that it increases the molecular weight of the gas **502**, something that may prove advantageous in reducing the cost of the expansion **514** and/or of the compression **924**. What actually happens is that when these gases are very rich in hydrogen, it is not easy for these gases to be compressed/expanded using the technologies best suited to high flow rates, namely technologies of the axial, radial or supersonic shockwave type. It then becomes necessary to use technologies of the positive-displacement type, for example using pistons or screws, which are very expensive to implement.

[0165] FIG. 12 schematically depicts the use of a method according to the invention in a plant producing synthesis gas from steam reforming. A carbon product **902** (natural gas, methanol, naphtha, etc.) is introduced into a reactor **900**.

[0166] The synthesis gases **903** produced in the reactor **900** chiefly comprise the compounds CO, CO₂, H₂ and H₂O. The fluid **905** may potentially be compressed by a compressor **101**, cooled in an exchanger **105** and dried in a dryer **107** before entering a low-temperature exchanger **109** where it may be partially liquefied at a temperature close to that of the triple point for CO₂. The diphasic gas-liquid fluid **912** obtained is separated into a gaseous fraction **502** and a liquid fraction **920** in the separator **928**. The gaseous fraction **502** is then cooled by a near-isentropic expansion, for example in a turbine **514**, so as to obtain a gas-solid diphasic mixture **503**. This is separated into a gaseous fraction **44** and a CO₂-rich solid fraction **62** in the vessel **111**. The solid fraction **62** is mixed with the liquid **920** in the bath **121**, which is heated with gas **74** produced by the vaporizing of the liquid **72** in the exchanger **109**. The liquid CO₂ **64** is compressed by a pump and heated up in the exchanger **109** without vaporizing or pseudo-vaporizing if the pressure is above the supercritical pressure. The lean gas **44** can then be purified in terms of CO₂ at a low temperature, for example by adsorption using a molecular sieve 13X before being introduced into a cryogenic unit **924** for the production of CO. This unit operates, for example, by methane scrubbing or partial condensation of the CO. This unit **924** produces a hydrogen-enriched gas **929** and a CO-enriched gas **925**. One or more fluids of this unit may be compressed at low temperature, then reintroduced into the heat exchanger **926**.

[0167] In this case, solid cryo-condensation replaces elimination of CO₂ by absorption with amines (MDEA or MEA). If there is a desire to produce pure hydrogen, then it is possible to add an H₂ PSA into this scheme either upstream of this solid cryo-condensation purification, that is to say on the outlet side of the reformer **900** after the cooling of the synthesis gas, or on the H₂-rich gas **929**.

[0168] It might be supposed that these solid cryo-condensation methods are deficient in cold. In actual fact, this is not the case at all. On the contrary, these solid cryo-condensation methods with near-isentropic expansion of the process gas produce excessive amounts of cold, especially if the method also provides external work. The problem is then that the CO₂-rich fluids and the CO₂-lean gas exit at low temperature, which represents an appreciable energy loss. In order to minimize the energy consumption of this method, one or more of the following operations may be carried out:

[0169] internally:

[0170] cold compression of one of the fluids of the cryo-condensation method:

[0171] process gas cooled to low temperature prior to compression;

[0172] CO₂-lean gas that is compressed at low temperature (cf. FIG. 2). It can then either be expanded again or compressed under vacuum to return it to atmospheric pressure or it can be expanded after it has been heated in the hot part of the method that produced the process gas;

[0173] indirect solid cryo-condensation in an exchanger;

[0174] externally:

[0175] cold compression of any fluid of the plant;

[0176] production of liquid nitrogen and/or liquid air;

[0177] transcritical Rankine cycle on the CO₂

[0178] FIG. 13 schematically depicts the use of a method according to the invention implementing a transcritical Rankine cycle on the CO₂. It also includes the features of a method in which a liquid cryo-condensation and then a solid cryo-condensation are performed in succession and in which the purity of the CO₂ produced is improved using two distillation columns, one of them to eliminate the compounds less volatile than CO₂ (NO₂ or N₂O₄, SO₂, etc.) and another to eliminate the compounds that are more volatile.

[0179] The fluid **24** consists of flue gases and may be at a temperature of the order of 150° C. and is injected into a filter **103** to remove the particles down to a concentration level of below 1 mg/m³, preferably below 100 µg/m³.

[0180] The dust-free fluid **30** is cooled to a temperature of close to 0° C., generally of between 0° C. and 10° C., so as to condense the water vapor it contains. This cooling is carried out in a tower **105b**, with water injected at two levels, cold water **36b** and water **34b** at a temperature close to the wet bulb temperature of the ambient air. It is also possible to conceive of indirect contact. The tower **105** may or may not have packings. This tower may also serve as a scrubbing tower for the SO₂.

[0181] On leaving this first tower, the fluid that may have been desaturated, is compressed to a pressure of between 5 and 50 bar abs in the compressor **101**. The fluid **32** is cooled to a temperature close to 0° C. and generally of between 0° C. and 10° C. so as to condense the water vapor it contains. This cooling is carried out in a tower **105** with water injected at two levels, cold water **36** and water **34** at a temperature close to the wet bulb temperature of the ambient air. It is also possible to conceive of indirect contact. The tower **105** may or may not have packings.

[0182] The fluid **38** is sent to a unit **107** that eliminates the residual water vapor, for example using one and/or another of the following methods:

[0183] Adsorption on fixed beds, fluidized beds and/or rotary dryer, it being possible for the adsorbent to be activated alumina, silica gel or a molecular sieve (3A, 4A, 5A, 13X, etc.);

[0184] Condensation in a direct-contact or indirect-contact exchanger.

[0185] The process fluid **40** is cooled then brought into contact in a distillation column **79** with pure CO₂, so as to recover the compounds less volatile than CO₂ in the form of a liquid containing CO₂ and, for example, NO₂ (or its dimer N₂O₄). This liquid can be pumped and vaporized in the unit **78**, then sent either to a combustion chamber to reduce the

NO₂ or to the unit for purifying the stream **30** by low-pressure scrubbing of the SO₂, where it acts as a reagent, either directly in the form of NO₂ or in the form of nitric acid having been reacted with water.

[0186] The process fluid **74a** is then cooled and partially condensed into liquid form and sent to the separator **76**. The liquid fraction **76a** is sent to the bath **121**. The gaseous fraction **76b** is sent to an expansion turbine so as there to produce a gas-solid diphasic stream **42** which is then sent to the vessel **111** where it is separated into a CO₂-lean gas **44** and solid CO₂ **62**. An auxiliary fluid **93**, for example from an air gas separation unit, may potentially supply additional cold for solid cryo-condensation. When it does, it may be advantageous to tap from the CO₂-lean gas **44** a fluid **92** which returns to the unit that supplied the fluid **93**. The solid **62** is compressed for example by an endless screw and injected into the bath **121** of liquid CO₂, from which a liquid **64** is tapped. This liquid may potentially be pumped and introduced into a distillation column **75** where its compounds more volatile than CO₂ are eliminated. The pure liquid **68** is heated up without vaporizing or pseudo-vaporizing if it is supercritical. It may once again be pumped to obtain the fluid **5** ready for transport. A part of the fluid **5** may be tapped off to be vaporized or pseudo-vaporized in a unit **72**. This unit **72** is, for example, any arbitrary source of heat of the plant that produces the process fluid. This part of the fluid **80** is then expanded in a turbine **73** used to produce electricity or mechanical power and is then cooled in the exchanger **109** and condensed by direct exchange in the bath **121**, at the same time melting the solid CO₂.

[0187] On leaving the exchanger **109**, the fluid **48** can still notably be used to regenerate the unit that eliminates residual vapor **107** and/or for producing cold water **36a** by evaporation in a direct-contact tower **115** into which a dry fluid **50** is introduced and becomes saturated with water, vaporizing part of it. Potentially, the cold water may undergo additional cooling in a refrigerating unit **119**. Thereafter, this cold water can be used in one and/or other of the towers **105** and **105b** to cool the process gas before and/or after compression.

[0188] FIGS. **14** and **15** depict a turbine for carrying out near-isentropic expansion of the process fluid with the production of external work in accordance with the invention. The upstream stator part **960** begins with the volute (not depicted) followed by vanes **950** which may be fixed or variable. Next comes the rotor part **960** which, for example, comprises blades **952** with a leading edge **951** where the rotor part **960** begins and a trailing edge **954** where it ends.

[0189] Downstream of the rotor part, if centrifugal force is not to be used on the solid parts, the rotor part may consist of a simple deceleration cone.

If the downstream stator part **961** is to be used to achieve a first separation, then the fact that the fluid has been made to rotate in the rotor part and the centrifugal effect can be used to separate a CO₂-rich fraction at the periphery from a CO₂-lean fraction at the center. It may also be advantageous to increase the speed and therefore perform an additional expansion of the fluid in a convergent nozzle **956** (a so-called "Laval" turbine). By reducing the pressure before decelerating the gas, the amount of solidified CO₂ can be increased. Most of the CO₂-lean gas is recovered at the center of the flow **959** and most of the solid CO₂ is recovered at the periphery **958**, mixed in with a fraction of gas.

1-15. (canceled)

16. A method for producing at least one CO₂-lean gas and one or more CO₂-rich primary fluids from a process fluid containing CO₂ and at least one compound more volatile than CO₂ comprising:

- a) a first cooling of said process fluid by exchange of heat with no change in state;
- b) a second cooling of at least part of said process fluid cooled in step a) so as to obtain at least one solid containing predominantly CO₂ and at least said CO₂-lean gas; and
- c) the liquefaction and/or sublimation of at least part of said solid and making it possible to obtain said one or more CO₂-rich primary fluids;

wherein at least part of the cold required to perform said first cooling and/or said second cooling is supplied by one or more refrigerating cycles each comprising at least one near-isentropic expansion of a gas.

17. The method of claim **16**, wherein said refrigerating cycles each comprising at least one near-isentropic expansion employ working fluids chosen from the following:

- an auxiliary fluid containing nitrogen and/or argon and/or a mixture of air gases;
- a fluid comprising all or some of said CO₂-lean gas) or derived from all or part of said CO₂-lean gas; and/or
- a fluid comprising all or part of said process fluid or derived from all or part of said process fluid.

18. The method of claim **16**, wherein at least part of the cold required for performing said second cooling is supplied by exchange with:

- the working fluid of one of said refrigerating cycles each comprising at least one near-isentropic expansion;
- an auxiliary fluid containing nitrogen and/or argon and/or a mixture of air gases;
- a fluid containing all or part of said CO₂-lean gas or derived from all or part of said CO₂-lean gas; and/or
- a fluid containing all or part of said process fluid or derived from all or part of said process fluid.

19. The method of claim **18**, wherein at least part of the cold needed to carry out said second cooling is supplied by direct exchange.

20. The method of claim **17**, wherein at least one of said refrigerating cycles each comprising at least one near-isentropic expansion employs all or part of said process fluid as working fluid.

21. The method of claim **16**, wherein at least one of said refrigerating cycles each comprising at least one near-isentropic expansion comprises at least one near-isentropic expansion supplying external work.

22. The method of claim **21**, further comprising a step d) of heating up at least one of said CO₂-rich primary fluids and/or said CO₂-lean gas by cold compression and/or by exchange of heat with an auxiliary fluid.

23. The method of claim **20**, wherein said near-isentropic expansion of at least one of said refrigerating cycles each comprising at least one near-isentropic expansion comprises one or more of the following steps:

- causing the process fluid to rotate about an axis substantially parallel to the direction of flow of said process;
- raising the speed of the process fluid;
- separating the solid CO₂ from the process fluid using a centrifugal effect;
- decelerating the gas that has become CO₂-lean.

24. The method of claim **16**, wherein, in step b), at least part of said process fluid cooled in step a) is cooled in such a way as further to obtain a liquid comprising predominantly CO₂.

25. The method of claim **16**, wherein said process fluid comes from industrial flue gases.

26. The method of claim **16**, wherein said process fluid comes from a steel-making plant.

27. The method of claim **26**, wherein:

said process fluid comes at least partially from a blast furnace; and

said CO₂-lean gas is at least partially recirculated into said blast furnace.

28. The method of claim **16**, wherein said process fluid comes at least partially from a refinery and/or from a chemical plant.

29. The method of claim **28**, wherein said process fluid comes at least partially from the gasification and/or the partial oxidation and/or an oxygen reforming of a given carbon fuel.

30. The method of claim **26**, wherein:

said process fluid comes from a plant comprising an air separation unit; and

said near-isentropic expansion of at least one of said refrigerating cycles each comprising at least one near-isentropic expansion of a gas is carried out in said air separation unit.

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