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Saysset et al.(10) **Pub. No.: US 2008/0302133 A1**(43) **Pub. Date: Dec. 11, 2008**(54) **METHOD AND DEVICE FOR RECOVERING
CARBON DIOXIDE FROM FUMES****Publication Classification**(75) Inventors: **Samuel Saysset**, Asnieres sur Seine
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BOSTON, MA 02109 (US)(57) **ABSTRACT**

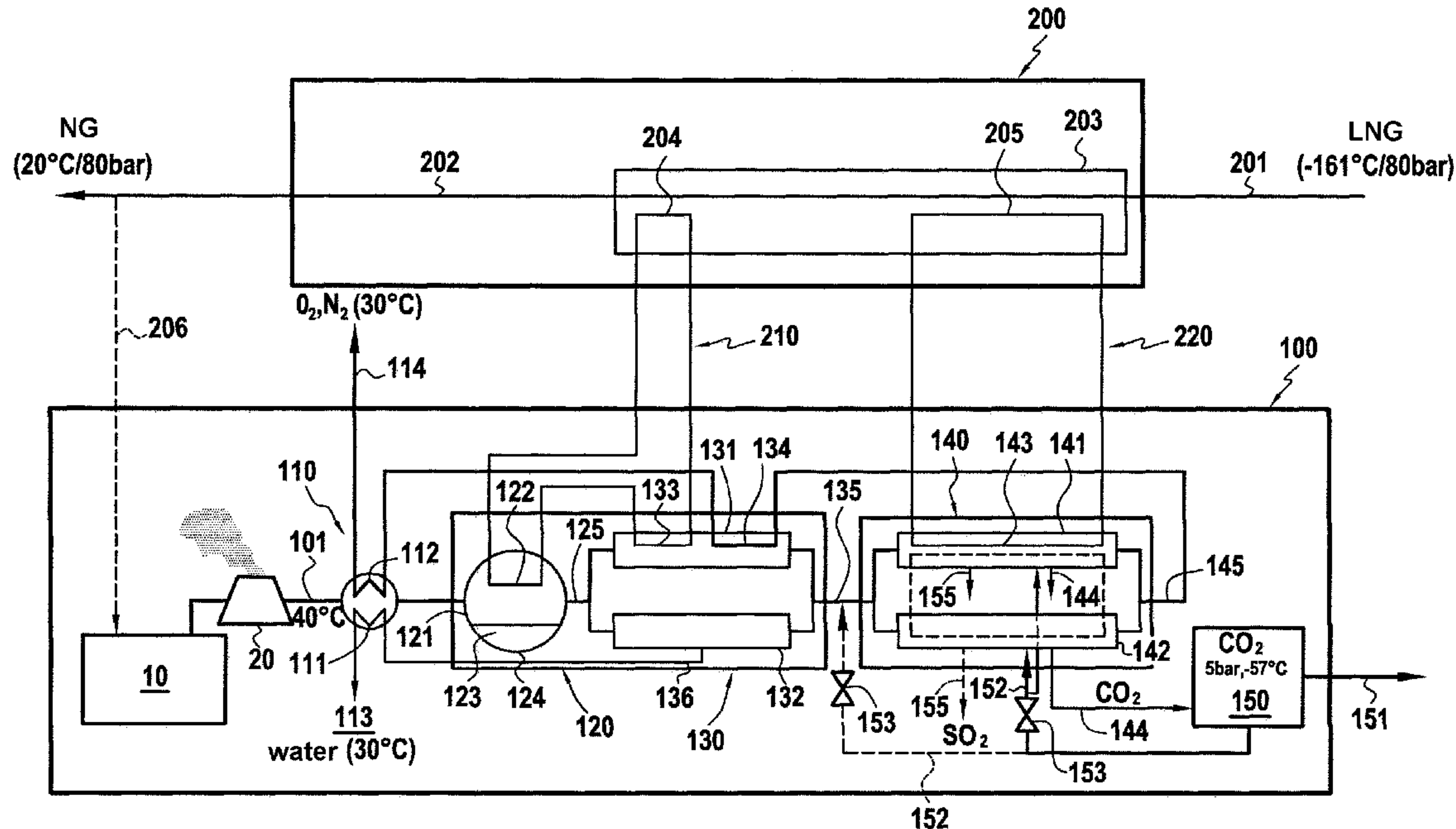
The method and the system for capturing the carbon dioxide present in flue-gas implement a) a first cooler device (110, 120) for cooling flue-gas and comprising at least one heat exchanger (122) for eliminating a fraction of the water present in the flue-gas by condensation; b) a flue-gas dehydration device (130); c) a second cooler device (140) for cooling the flue-gas and comprising at least one heat exchanger (141, 142) for bringing the flue-gas to a temperature that causes anti-sublimation of the carbon dioxide present in the flue-gas; d) a heater device (141, 142) in a closed enclosure for heating the solidified carbon dioxide to cause it to melt; and e) a device (144) for drawing off or pumping liquid and/or gaseous carbon dioxide to a thermally insulated tank (150). The system further comprises an expander device (152, 153) for expanding a portion of the recovered liquid carbon dioxide to atmospheric pressure, and for reinjecting said portion of the carbon dioxide into the flue-gas at the second flue-gas cooler means (140).

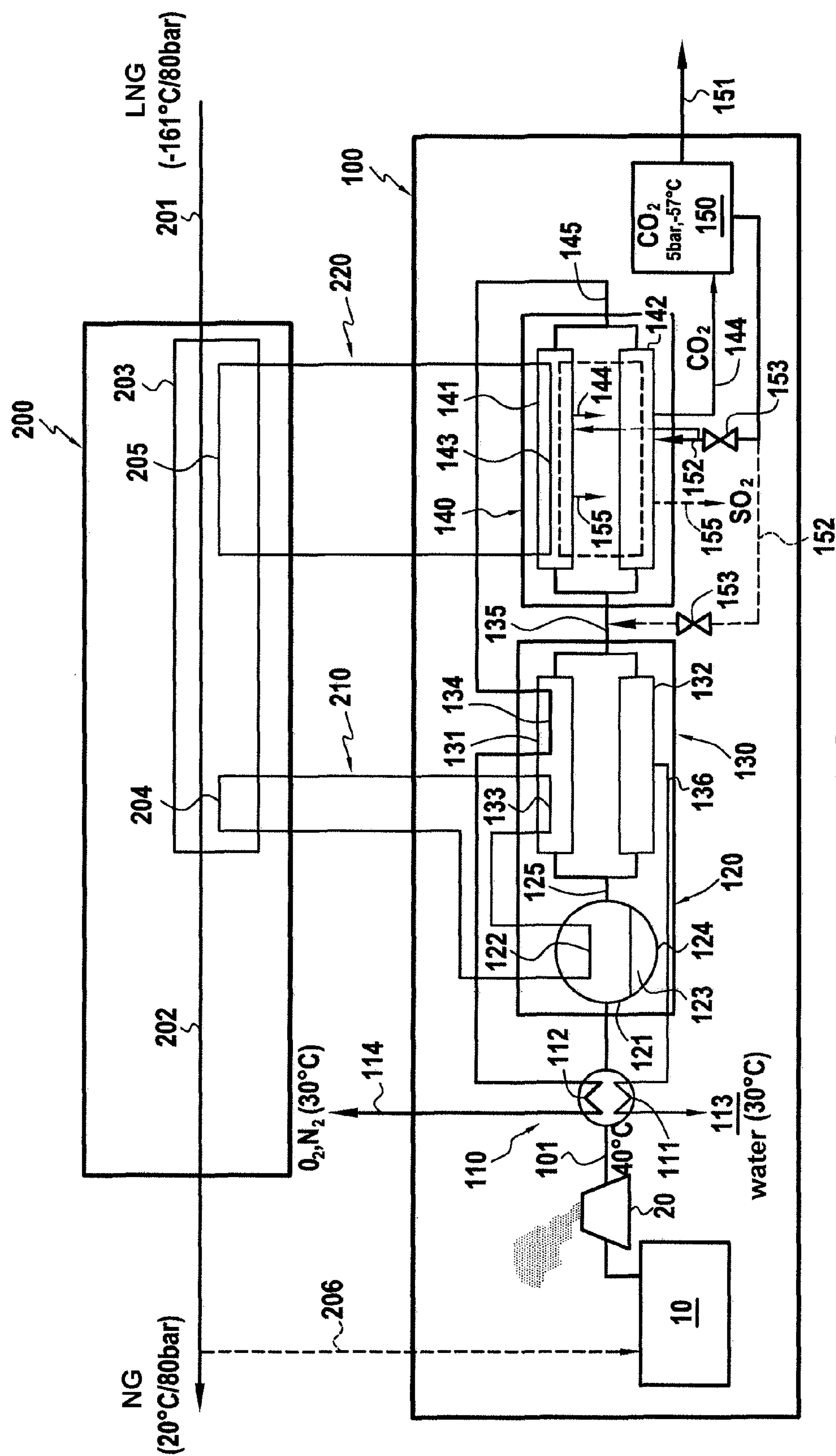
(73) Assignee: **GAZ DE FRANCE**, Paris (FR)(21) Appl. No.: **12/158,523**(22) PCT Filed: **Dec. 20, 2006**(86) PCT No.: **PCT/FR2006/051400**

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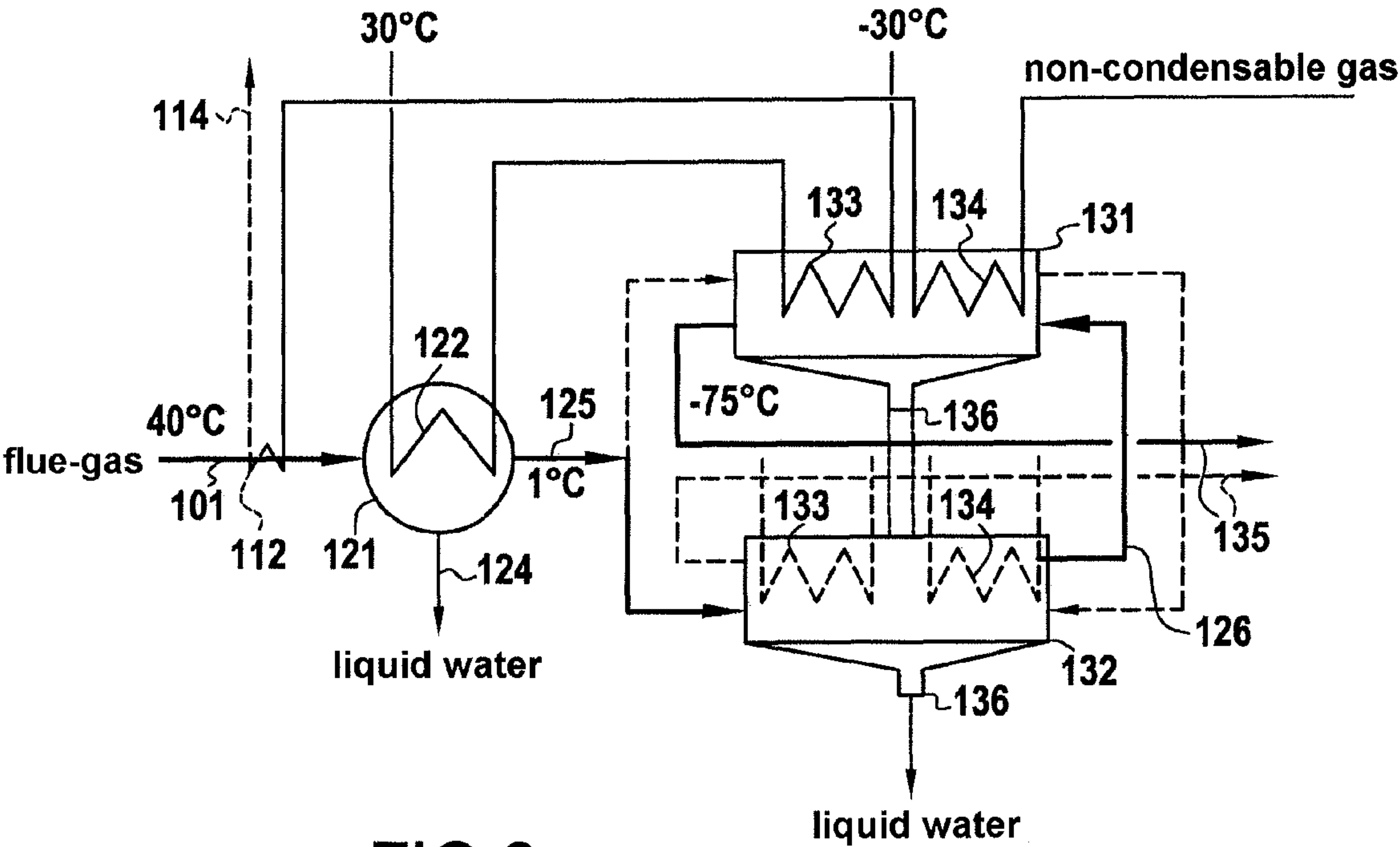


FIG.2

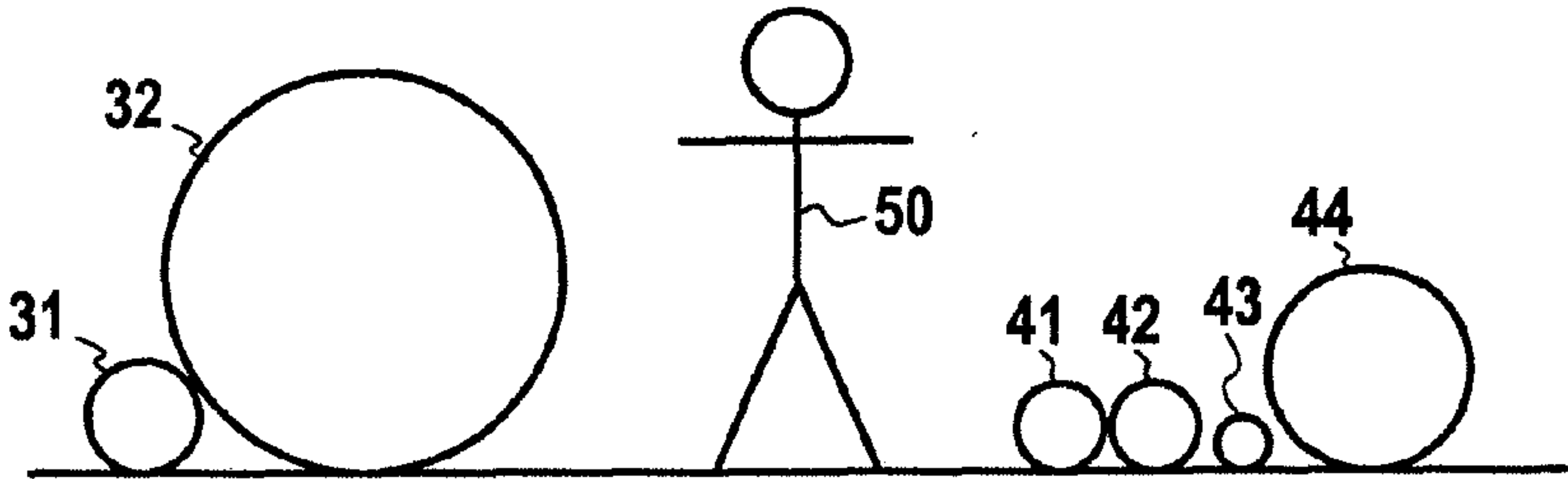


FIG.3

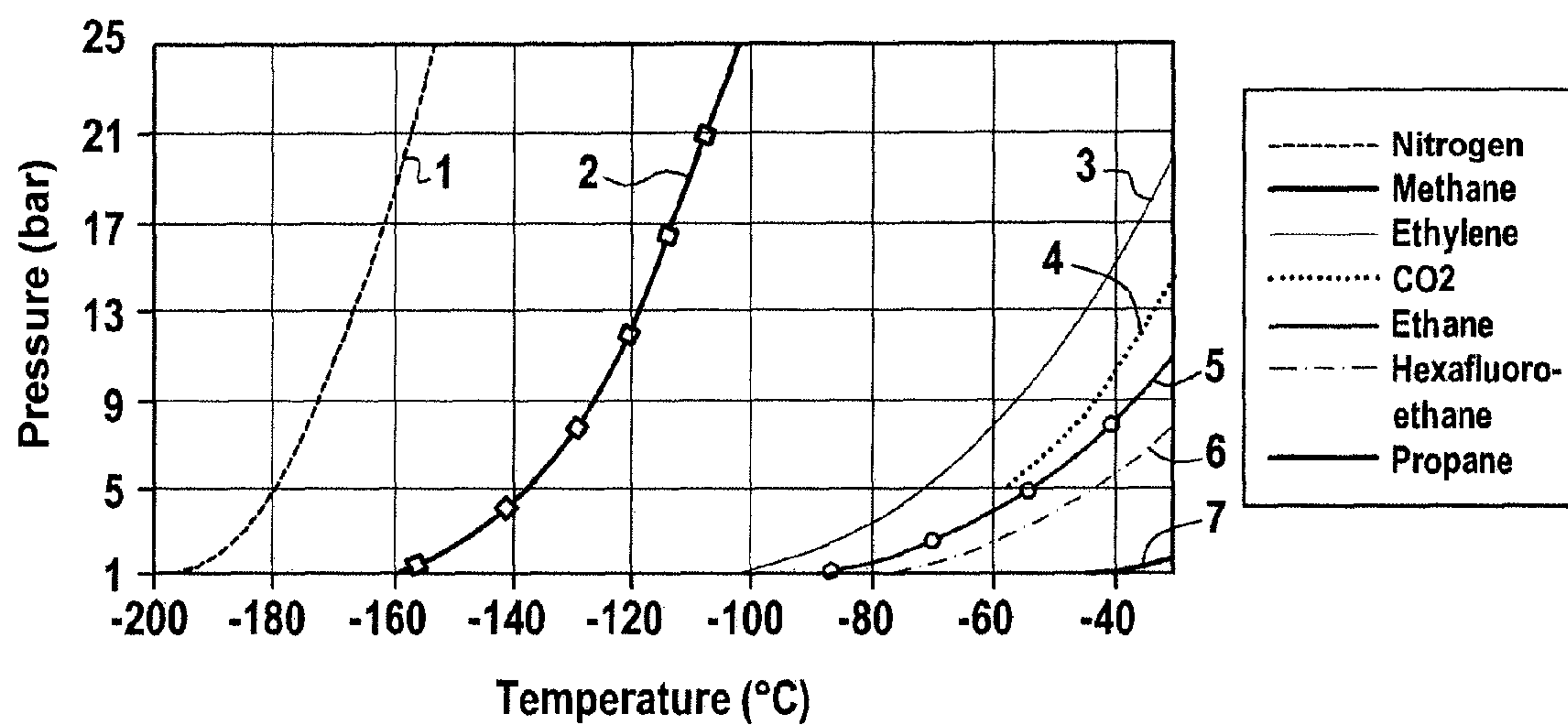


FIG.4

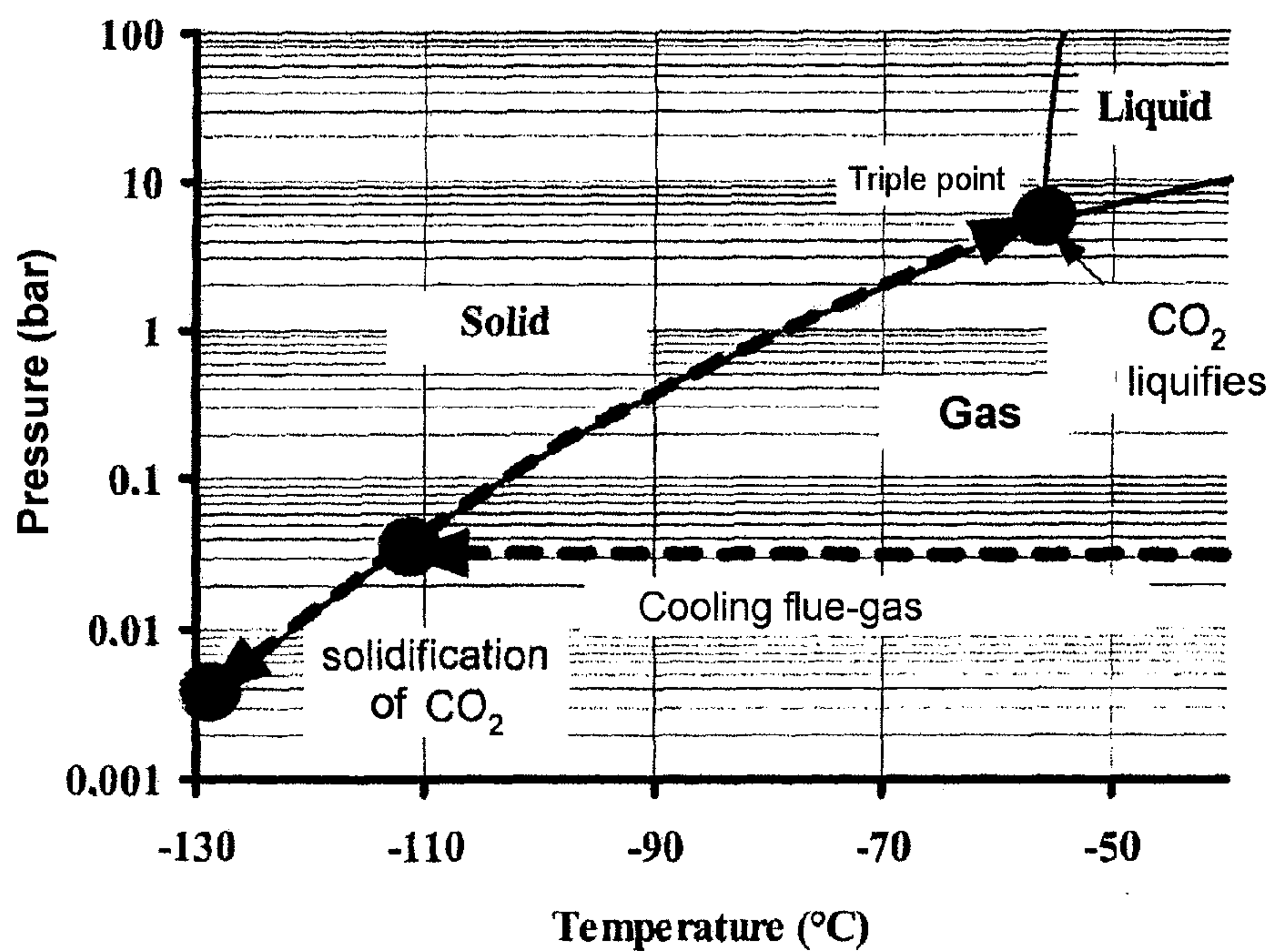


FIG.5

METHOD AND DEVICE FOR RECOVERING CARBON DIOXIDE FROM FUMES

[0001] The present invention relates to a method and a system for capturing the carbon dioxide (CO₂) contained in flue-gas or in other gaseous effluent coming from industrial installations.

[0002] Capturing carbon dioxide and storing it geologically presents an opportunity for reducing the emission of greenhouse-effect gases, in addition to efforts at improving energy efficiency and inciting the use of non-fossil resources.

[0003] At present, the cost of capturing CO₂ constitutes about three-quarters of the total cost of the system for geologically sequestering CO₂, including capturing, transporting, and storing CO₂.

[0004] Furthermore, energy consumption represents about 50% of the cost of capture.

[0005] In particular, amongst the technologies that can be envisaged for capturing CO₂, low-temperature or “cryogenic” distillation suffers from the drawback of consuming a large amount of energy in order to achieve low temperatures.

[0006] There thus exists a need to rationalize the operation of CO₂ capture in order to improve the effectiveness of that operation and reduce its cost.

[0007] The term “anti-sublimation” is used below to designate the physical phenomenon of solid condensation whereby a gas changes state and passes directly into the solid phase without liquefaction taking place, i.e. without passing via the liquid state. Anti-sublimation thus constitutes the physical phenomenon that is the inverse of sublimation which designates a body passing directly from the solid state to the gaseous state without passing via the liquid state.

[0008] Various methods and systems for capturing CO₂ by liquefaction or anti-sublimation have already been proposed.

[0009] When carbon dioxide is at a partial pressure of more than 5.18 bar, it is possible to obtain direct liquefaction of CO₂ by cooling flue-gas. That type of method nevertheless presents the drawback of requiring effluents to be available under pressure or flue-gas to be compressed.

[0010] When CO₂ is available at a partial pressure of less than 5.18 bar, as is true of combustion gas, cooling the flue-gas will lead to anti-sublimation of CO₂. The solid carbon dioxide can then be handled in solid form, e.g. after being separated in a cyclone, or it can be sublimed prior to being subsequently liquefied downstream, or else it can be melted directly merely by being heated.

[0011] Document EP 1 355 716 B1 and patent application WO 2004/080558 disclose a method of extracting CO₂ from flue-gas by cooling and solidifying CO₂ at atmospheric pressure by extracting heat by means of fractionated distillation.

[0012] Nevertheless, in some circumstances, in particular for flue-gas coming from a gas turbine or a gas boiler, the CO₂ content of the flue-gas can be quite low, e.g. about 1% to 5%, which implies a starting temperature for anti-sublimation at atmospheric pressure that can be of the order of -110° C. to -120° C.

[0013] Furthermore, this CO₂ content in flue-gas decreases with increasing target capture ratio.

[0014] When forming a solid from a gaseous phase it is also observed that anti-sublimation is delayed at low temperature and at low partial pressure, in particular with CO₂. This phe-

nomenon gives rise to anti-sublimation of the compound at a temperature lower than the temperature specified by thermodynamics.

[0015] Because of this phenomenon, in order to anti-sublime CO₂, it is therefore necessary either to cool the compound below its thermodynamic anti-sublimation temperature, which amounts to having an even lower operating temperature in the heat exchanger, or else to increase the heat exchange surface area, thereby increasing the amount of contact between the compound and cold surfaces. Both of those two conditions increase the cost of the method.

[0016] The present invention seeks to remedy the above-mentioned drawbacks and to enable CO₂ to be captured in a manner that is effective, but at reduced cost, and with installations that are simplified, and with efficiency that is potentially improved.

[0017] According to the invention, these objects are achieved by a method of capturing the carbon dioxide present in flue-gas, the method comprising the following steps:

[0018] a) first cooling of the flue-gas in order to eliminate a fraction of the water present therein by condensation;

[0019] b) dehydrating the flue-gas in order to eliminate the residual water;

[0020] c) second cooling of the flue-gas by heat exchange so as to bring it to a temperature such that carbon dioxide passes directly from the gaseous state to the solid state by anti-sublimation;

[0021] d) after removing the flue-gas, heating the solidified carbon dioxide in a closed enclosure up to the triple point where a liquid phase appears; and

[0022] e) drawing off or pumping out the liquid and/or gaseous carbon dioxide to a thermally insulated tank;

[0023] the method being characterized in that a fraction of the recovered liquid carbon dioxide is recycled, and after expanding to atmospheric pressure, is reinjected during the second cooling step in continuous or intermittent manner in order to be mixed with the flue-gas previously delivered by the dehydration step.

[0024] In order to combat the delay in anti-sublimation, it is possible to encourage the kinetics of the anti-sublimation process by injecting CO₂ crystals that perform a seeding function for solid formation. Such fine solid particles constitute nucleation centers on which gaseous CO₂ solidifies. The reinjection can take place within the heat exchanger, starting from the point where the temperature of the flue-gas is close to the theoretical anti-sublimation temperature.

[0025] The recovered fraction of the liquid carbon dioxide that is recycled is thus reinjected during the second cooling step, preferably in the form of fine solid particles, and also preferably into the inside of a heat exchanger.

[0026] In a particular implementation, the method further comprises a step of pre-cooling the flue-gas prior to said first cooling step, the pre-cooling step being performed by exchanging heat with at least one of the fluids comprising the liquid water recovered during the first cooling step and the flue-gas dehydration step, and the non-condensable compounds from the flue-gas that are recovered after said second cooling step.

[0027] In a particular advantageous implementation, the first cooling of the flue-gas, the dehydration of the flue-gas, and the second cooling of the flue-gas make use of heat exchange with the flue-gas via cooling loops operating by

heat exchange with the liquefied natural gas (LNG) that is present in a methane terminal for regassification, and that is used as a cold source.

[0028] According to a particular characteristic, the first cooling of the flue-gas and the dehydration of the flue-gas are performed by exchanging heat with the flue-gas via at least one cooling loop making use of glycol-containing water.

[0029] According to another particular characteristic, the second cooling of flue-gas makes use of heat exchange with the flue-gas via at least one cooling loop making use of methane or of nitrogen.

[0030] Under such circumstances, according to yet another particular characteristic, the second cooling of flue-gas makes use of heat exchange with the flue-gas via at least one additional cooling loop making use of ethylene or ethane.

[0031] When LNG is available at a methane terminal for regassifying natural gas, making use of the LNG as a cold source is particularly advantageous since the low temperature of the LNG is thus used advantageously for purposes of industrial and energy optimization, with the flue-gas from which the CO₂ is to be extracted then constituting the hot source for intermediate-fluid heat exchangers that enable the LNG that is stored in liquid form at -161° C. and at a pressure of 80 bar to be regassified.

[0032] When an industrial installation that gives off CO₂, such as a fossil fuel fired power station is located close to a methane terminal in which LNG is regassified, it is therefore entirely appropriate to make use of the LNG as a cold source in the operation of capturing CO₂ from the combustion gas or from gaseous effluents, by anti-sublimation at approximately atmospheric pressure, followed by melting at a pressure of a few bar, which can be obtained merely by heating the solid CO₂.

[0033] The invention is applicable to any flue-gas from power stations and other thermal installations (steel works, cement works, . . .) that make use of a variety of fossil fuels (natural gas, coal, oil, . . .) and that contain various concentrations of CO₂, even concentrations that are low and less than 1%.

[0034] Furthermore, by using various cooling loops involving different fluids and producing staged cooling of the flue-gas, it is possible to reduce very significantly the dimensions of the pipes in the final cryogenic loop that involves very low temperatures (e.g. using nitrogen), even if the distance between the methane terminal and the CO₂ capture installation is several hundreds of meters or several kilometers.

[0035] The method of the invention may present various other advantageous characteristics depending in different particular implementations:

[0036] Flue-gas dehydration includes a step of exchanging heat with the non-condensable compounds of the flue-gas recovered after the second cooling step.

[0037] The flue-gas dehydration step is performed discontinuously, alternating between a step of cooling the flue-gas to solidify water on the walls of a heat exchanger, and a step of heating the solidified water in order to enable it to be recovered in liquid form.

[0038] The solidified water is heated by exchanging heat with flue-gas, prior to gas being cooled during the step of cooling flue-gas with solidification of water.

[0039] The second flue-gas cooling step for giving rise to anti-sublimation of carbon dioxide, and the step of heating the solidified carbon dioxide are performed discontinuously and in alternation.

[0040] The step of heating the solidified carbon dioxide up to the triple point where a liquid phase appears can be performed by exchanging heat with the flue-gas prior to cooling it during the second flue-gas cooling step.

[0041] The method further includes a step of recovering sulfur oxides contained in the flue-gas by anti-sublimation and by heating up to the triple point where a sulfur oxide liquid phase appears.

[0042] The invention also provides a system for capturing carbon dioxide present in flue-gas, the system comprising:

[0043] a) first cooler means for cooling flue-gas and comprising at least one heat exchanger for eliminating a fraction of the water present in the flue-gas by condensation;

[0044] b) flue-gas dehydration means;

[0045] c) second cooler means for cooling flue-gas and comprising at least one heat exchanger for bringing the flue-gas to a temperature that causes anti-sublimation of the carbon dioxide present in the flue-gas;

[0046] d) heater means for heating the solidified carbon dioxide in a closed enclosure in order to cause it to melt; and

[0047] e) means for drawing off or pumping the liquid and/or gaseous carbon dioxide to a thermally insulated tank;

[0048] the system being characterized in that it further comprises expander means for expanding a fraction of the recovered liquid carbon dioxide to atmospheric pressure and for reinjecting said fraction of the carbon dioxide into the flue-gas at said second flue-gas cooler means. The system preferably further includes means for reinjecting said recovered fraction of the liquid carbon dioxide in the form of fine solid particles into the flue-gas.

[0049] In a particular embodiment, the first cooler means comprise a heat exchanger between the flue-gas and at least one of the fluids comprising the liquid water recovered in the first cooler means or in the flue-gas dehydration means, and the non-condensable compounds of the flue-gas recovered at the inlet to the second cooler means.

[0050] In an advantageous application, the system of the invention includes cooling loops using heat-transferring fluids flowing firstly in heat exchangers present in a methane terminal for exchanging heat with the liquefied natural gas subjected to a regassification process, and secondly in heat exchangers placed in at least one of the first cooler means, the dehydration means, and the second cooler means in order to exchange heat with the flue-gas, giving rise to capture of carbon dioxide.

[0051] According to a particular characteristic, the system includes at least one cooling loop using glycol-containing water as its heat-transferring fluid and including at least one heat exchanger disposed in the first cooler means to the dehydration means.

[0052] According to another particular characteristic, the system includes at least one cooling loop using methane or nitrogen as its heat-transferring fluid and including at least one heat exchanger disposed in the second cooler means.

[0053] Under such circumstances, in a particular embodiment, the system may further comprise at least one cooling loop using ethylene or ethane as its heat-transferring fluid and including at least one heat exchanger disposed in the second cooler means.

[0054] The system may comprise means for recovering non-condensable compounds from the flue-gas at the outlet from the second cooler means, and means for exchanging heat with at least one of the flue-gas dehydration means.

[0055] In a particular embodiment, the flue-gas dehydration means comprise at least first and second enclosures provided with heat exchangers and capable of receiving flue-gas discontinuously so that each of them can act in turn to cool flue-gas and solidify the water contained therein on the walls of the corresponding enclosure, and to heat the solidified water in order to enable it to be recovered in liquid form.

[0056] According to another particular aspect of the invention, the second flue-gas cooler means and said heater means comprise at least first and second enclosures provided with heat exchangers and capable of receiving flue-gas discontinuously in such a manner that each of them in turn cools flue-gas with anti-sublimation of the carbon dioxide that is deposited on the walls of the corresponding enclosure, and heats the solidified carbon dioxide in order to cause it to melt.

[0057] The system may also include means for recovering sulfur oxides in the heater means in a closed enclosure.

[0058] Other characteristics and advantages of the invention from the following description of particular embodiments, given with reference to the accompanying drawings, in which:

[0059] FIG. 1 is a diagrammatic overall view of a system for capturing CO₂ by anti-sublimation in accordance with the invention;

[0060] FIG. 2 is a detail view showing the principle of a unit for dehydration by solidification/melting and suitable for incorporation in the system of FIG. 1;

[0061] FIG. 3 is a diagrammatic view comparing the sizes of cryogenic loops when using a single loop and when using two loops;

[0062] FIG. 4 is a graph plotting gas-liquid equilibrium curves for various compounds as a function of temperature and pressure; and

[0063] FIG. 5 is a CO₂ pressure-temperature diagram showing how CO₂ varies during a capture method of the invention.

[0064] An embodiment of the present invention is described with reference to FIG. 1.

[0065] Nevertheless, reference is made initially to FIG. 5 which shows the thermodynamic phenomenon that is used, namely anti-sublimation of CO₂ followed by compression/melting obtained merely by heating solid CO₂.

[0066] As mentioned above, this phenomenon is applicable to the flue-gases from fuel-burning installations and power stations that make use of a variety of fossil fuels (natural gas, coal, oil, . . .), the flue-gases containing varying concentrations of CO₂ that may lie in the range less than 1% to concentrations of several tens of percent.

[0067] Table 1 gives examples of typical compositions for gas turbine flue-gases.

TABLE 1

Gas turbine flue-gas composition				
	N ₂	H ₂ O	O ₂	CO ₂
Low molar composition, wet (%)	76	6	14	4
Low molar composition, dry (%)	81	—	15	4

[0068] As can be seen, after water has been eliminated, the flue-gas contains about 4% CO₂ (at a partial pressure of 0.04 bar).

[0069] The flue-gas can then be cooled in a heat exchanger until CO₂ condenses as from −110° C. (see horizontal dashed line in FIG. 5).

[0070] The solid CO₂ trapped in the heat exchanger can then be heated and taken to the conditions of the CO₂ triple point where liquid CO₂ can be eliminated so as to move the thermal equilibrium in favor of producing liquid CO₂ (see top dashed-line curve in FIG. 5).

[0071] The temperature at which the anti-sublimation process begins depends on the CO₂ content of the flue-gas. Thus, it varies over the range −78.5° C. for pure CO₂ at atmospheric pressure, to −121.9° C. for effluent containing CO₂ at a partial pressure of 0.01 bar (see Table 2).

TABLE 2

Temperatures at which the CO ₂ anti-sublimation process begins as a function of the CO ₂ contents of flue-gas at atmospheric pressure							
CO ₂ content	100	15	10	5	2	1	0.1
Anti-sublimation temperature (° C.)	−78.5	−99.3	−103.1	−109.3	−116.7	−121.9	−136.7
Type of composition	Coal-fired plant		Gas boiler		Gas turbine		

[0072] In accordance with the invention, a fraction of the liquid CO₂ obtained at the outlet from the method is recycled by being expanded until fine solid particles are formed in the last heat exchanger so as to create nucleation centers.

[0073] This recycling enables the anti-sublimation heat exchanger to be optimized in terms of exchange area and final operating temperature.

[0074] FIG. 1 shows an advantageous example of an embodiment of the invention in the context of capturing flue-gas produced by an industrial installation 10. After cooling, e.g. in a conventional cooling tower 20, the combustion gas is available at a temperature of about 40° C. at the inlet to the CO₂ capture and processing installation 110.

[0075] In the example of FIG. 1, the industrial installation 10 is situated close to a methane terminal 200 (e.g. at a distance of the order of a few hundreds of meters to a few kilometers), which terminal 200 receives LNG e.g. at a temperature of −161° C. and at a pressure of 80 bar, via a line 201. The LNG passes through a heat exchanger 203 that exchanges heat between the LNG and heat-transferring fluids circulating through heat exchangers 204, 205 having cooling loops 210 and 220. At the outlet 202 from the methane terminal, the natural gas continues the regassification process. The regassified natural gas can be used for example to feed the industrial installation 10, such as a gas-fired power station, via a line 206.

[0076] The invention applies to capturing CO₂ from the combustion gas, however it can also be applied to capturing CO₂ from other gaseous effluents, for example synthesis gas obtained in a hydrogen-production context.

[0077] The invention also makes it possible, by using the same anti-sublimation method, to capture sulfur oxides (SO_x) that might be present in the flue-gas together with the CO₂.

[0078] In the FIG. 1 installation, the flue-gas acts as a hot source for the cooling loops **210**, **220**, while the LNG at -161°C . acts as a cold source.

[0079] The flue-gas delivered via the line **101** is cooled in several stages.

[0080] In a cooling device **120** comprising a heat exchanger **122**, with a cooling loop **210**, e.g. glycol-containing water, the combustion gas is cooled from 40°C . to 1°C . so as to cause a fraction **123** of the water present in the gas to condense as a liquid (liquefaction) in the enclosure **121**.

[0081] The condensed water **123** is removed via a pipe **124** and may be sent to a heat exchanger **111**, for example, in order to perform pre-cooling of the flue-gas prior to its entry into the cooling device **120**. The water heated in the heat exchanger **111** serves to bring the flue-gas temperature to 30°C ., for example, and it is then removed via a line **113** at a temperature that is close to ambient (30°C .).

[0082] The flue-gas coming from the cooling device **120** is introduced via a line **125** into a gas dehydration device **130**.

[0083] It is necessary to dehydrate the gas in order to eliminate residual water (about 0.6% water in the gas, assuming that the vapor pressure of water at 1°C . is 6.6 millibar (mbar)).

[0084] The residual water can solidify and might therefore block the installation downstream, and might then be found in the captured CO_2 .

[0085] The dehydration operation can also be performed by using the LNG from the methane terminal **200** as a cold source, e.g. in a heat exchanger **133** possibly suitable for being inserted in the same cooling loop **210** (e.g. using glycol-containing water) as the heat exchanger **122**.

[0086] The residual water can thus be solidified, e.g. at -30°C ., on the walls of at least one (**131**) of the two enclosures **131**, **132** that operate discontinuously in alternation (i.e. in batch mode).

[0087] When the water has solidified on the walls of one of the enclosures **131**, the gas is switched to the inlet of the other enclosure or of one of the other enclosures **131** so as to cause residual water to solidify in the same manner. At the same time, the water that has solidified on the walls of the first enclosure **131** is heated, e.g. making use of the heat in the gas by causing it to pass through the first enclosure **131** prior to penetrating into the second enclosure **132** where water capture is to take place.

[0088] This discontinuous operation in alternation of the enclosures **131** and **132** is shown in greater detail in FIG. 2.

[0089] In FIG. 2, it can thus be seen that water-saturated gas at 1°C . arriving via the line **125** penetrates initially into the enclosure **132** (in which the heat exchangers **133** and **134** are deactivated) for the purpose of melting the water that has solidified on the walls of that enclosure, with the liquid water being removed via a tube **136**. The gas is then conveyed via a pipe **126** to the capture enclosure **131** within which the heat exchangers **133** and **134** are activated so as to cool the gas and capture the residual water which solidifies on the walls of the enclosure **131**. The gas then leaves via a pipe **135** to be taken to the CO_2 capture stage. During the following alternation, the gas arriving via the pipe **124** is switched to the path drawn in dashed lines in FIG. 2 so as to penetrate initially into the enclosure **131**, where it causes the water to melt and be removed via the tube **136**, and from which the gas penetrates into the enclosure **132**, where the heat exchangers **133** and **134** are then activated so as to solidify the residual water. The

gas leaving the enclosure **132** is then transferred by the pipe **135** to the following stage for CO_2 capture.

[0090] In the enclosures **131**, **132**, it is possible to use a heat exchanger **134** as described above, forming part of a heat exchange cooling loop, e.g. using the LNG of a methane terminal as the cold source. It is also possible to make use of a heat exchanger **134** having non-condensable gas (nitrogen, oxygen, ...) flowing therethrough and recovered from the gas at the outlet **145** of the CO_2 capture process.

[0091] The non-condensable gas can likewise subsequently be transferred to a heat exchanger **112** acting, like the heat exchanger **111**, to pre-cool and eliminate condensed water in a stage **110** situated upstream from the cooler device **120** and the dehydration device **130**. The residual non-condensable gas (O_2 , N_2 , ...) can then be rejected into the atmosphere via a line **114** at a temperature of about 30°C . (FIGS. 1 and 2).

[0092] The liquid water removed by the tubes **136** can be used, like the water recovered by the pipe **124**, for pre-cooling in the heat exchanger **111**.

[0093] The gas present in the pipe **135** at the outlet from the dehydration stage **130** can present a temperature of about -30°C . and it penetrates into another cooler device **140** that may comprise one or more heat exchangers **143** forming part of cooling loops such as the loop **220** using the LNG present in the methane terminal **200** as a cold source.

[0094] The cooler device **140** comprises at least two enclosures **141**, **142**, each having a heat exchanger **143** forming part of the cooling loop **220**, together with means **144**, **155** for drawing off or pumping liquid and/or gaseous CO_2 , and possibly also sulfur dioxide.

[0095] The enclosures **141**, **142** operate in discontinuous manner in alternation in turns (i.e. they operate in batch mode) for capturing CO_2 (and possibly SO_2) by anti-sublimation and then for causing it to melt. Operation is similar to that described above with reference to FIG. 2 for capturing water.

[0096] Thus, after CO_2 (or SO_2) has been deposited on the walls of the enclosure **141** in which the heat exchanger **143** is active, the gas is switched to the enclosure **142**. Within the enclosure **141**, the heat exchanger **143** is deactivated and energy from the gas can be used to cause the temperature of the solid CO_2 to rise, e.g. from a temperature of -130°C . to a temperature of about -56.6°C ., with the CO_2 having a partial pressure of 5.18 bar, which corresponds to the triple point where the liquid and gaseous phases appear and coexist simultaneously (see FIG. 5). In order to shift the solid-liquid-gas equilibrium, it suffices to withdraw or pump out the CO_2 via a pipe **144** and deliver it to a thermally lagged tank **150** from which CO_2 can be taken via a pipe **151** for being transported to a temporary storage site, prior to being transported to and injected into an old oil field. During the melting of CO_2 , e.g. in the enclosure **141**, the gas passing through the other enclosure **142** leads to CO_2 being deposited by anti-sublimation in the enclosure **142**. The solidified CO_2 can then be melted during the following cycle of heating in the enclosure **142**, while the CO_2 capture phenomenon takes place in the enclosure **141**. The process of capture by anti-sublimation followed by recovery merely by melting sulfur dioxide present in the gas can be performed in a manner entirely similar to that described above with reference to CO_2 .

[0097] As mentioned above, an important characteristic of the invention lies in the fact that a fraction of the liquid CO₂ obtained on the line 144 at the outlet from the cooler device 140 and recovered in the tank 150 is recycled by a pipe 152 provided with a valve 153 either (dashed line) to the pipe 135 feeding dehydrated flue-gas to the inlet of the cooler device 140, or preferably (continuous lines) directly to the enclosures 141 and 142 in order to create nucleation centers for the anti-sublimation of CO₂.

[0098] As a result, it is possible to optimize the dimensioning of the cooling loop 220 operating with nitrogen or methane, the dimensioning of an optional additional loop using ethylene or ethane, and the dimensioning of the anti-sublimation heat exchangers 142 and 141 in terms of heat exchange area or CO₂ capture rate.

[0099] FIG. 4 plots gas/liquid equilibrium curves between -200° C. and -30° C. for various compounds that can be used as heat-transferring fluids in the cooling loops 210, 220. These compounds are nitrogen, methane, ethylene, CO₂, ethane, hexafluoroethane, and propane (curves referenced 1 to 7 respectively).

[0100] By using different cooling loops 210, 220 that implement different heat-transferring fluids and that lead to cooling in stages, it is possible to reduce the size of the cryogenic loop that uses nitrogen.

[0101] Thus, FIG. 3 shows relative to the size of an average individual 50, the size of a single nitrogen cryogenic loop using a pipe 31 for liquid nitrogen, and a pipe 32 for gaseous nitrogen return.

[0102] On the assumption that the energy needed for capturing 0.600 kilowatt hours per kilogram (kWh/kg) of CO₂ (which corresponds to exhaust gas from a gas turbine with recovery of energy, water, and non-condensables), the cooling power needed for capturing 320 (metric) tonnes (t) of CO₂ per hour is 192 megawatts (MW). On the basis of a nitrogen loop at 25 bar (-155° C. on the liquid side, and 30° C. on the gas side), the flow rate of nitrogen to be conveyed is more than one million normal cubic meters per hour (Nm³/h), giving a pipe diameter of 0.40 meters (m) for the pipe 31 on the liquid side assuming the speed of the liquid is 10 meters per second (m/s), (or of 0.70 m if the speed of the liquid is 3 m/s, for example), and a pipe diameter of 1.60 m for the pipe 32 on the gas side (10 m/s). A nitrogen loop of such a size can give rise to problems in operation (cryogenic fluid to be kept cold) and in terms of investment, in particular over distances of several kilometers.

[0103] In contrast, when use is made firstly of a cooling loop, e.g. with glycol-containing water 210 having go-and-return pipes 41 and 42, and also a nitrogen cooling loop 220 comprising a pipe 43 on the liquid side and a pipe 44 on the gas side, the dimensions of the various pipes, including the pipe 44 can be reduced.

[0104] As mentioned with reference to FIGS. 1 and 2, the flue-gas are dehydrated by cooling them from 40° C. to 1° C. so as to eliminate free water, and then to temperatures that are low enough to achieve the desired water contents. In the example described, the dehydration operation is performed by using a glycol-containing water cooling loop 210 that enables -40° C. to be reached, depending on the glycol content (ethylene glycol, propylene glycol).

[0105] Table 3 gives the water contents of the flue-gas and of the captured CO₂ as a function of the cooling temperature.

TABLE 3

Water contents of the flue-gas and of the captured CO ₂ as a function of the cooling temperature and for a capture rate of 100%		
Flue-gas cooling temperature (° C.)	Water content of flue-gas (ppm)	Water content of captured CO ₂ (ppm)
-30	490	1.3%
-40	180	0.5%
-50	60	1,650
-60	18	490
-70	5	130
-80	1	30
-90	0.1	5

[0106] With a dew point at -30° C., the water content of the flue-gas is thus 490 parts per million (ppm), i.e. about 5 grams (g) of water per kilogram (kg) of captured CO₂ (1.3%).

[0107] In order to avoid problems of corrosion and of hydrate formation during transport and injection into storage, it is preferable to dehydrate the flue-gas to a greater extent in order to obtain a water content in the CO₂ that is as low as 50 ppm.

[0108] For this purpose, the flue-gas can be cooled to about -75° C. by using an additional cooling loop in the gas dehydration portion.

[0109] This additional cooling loop may be a loop using LNG as its cold source and a heat-transferring fluid such as methane or ethylene.

[0110] Nevertheless, and as shown in FIG. 1, this additional loop is preferably a loop that makes use of the non-condensable gas available at the outlet 145 from the anti-sublimation stage so as to continue cooling the flue-gas in the heat exchanger 134 in order to obtain a temperature of about -75° C. at the outlet 135 from the dehydration device.

[0111] Table 4 gives numerical values for an example of a flue-gas dehydration installation in a cycle that combines 800 MW of natural gas, with a cooling power of 164 MW for performing dehydration, shared between the heat exchanger 122 (99 MW) and the heat exchanger 133 (65 MW). On the basis of a glycol-containing water loop at 1 bar (-40° C. cold side and 30° C. hot side), the flow rate of water that needs to be transported is about 2500 m³/h, giving a diameter of about 0.30 m for the pipes 41 and 42 in FIG. 3.

[0112] Table 4 gives the temperature, the pressure, and the flow rate for nitrogen, oxygen, argon, CO₂, and water at various points in the installation of FIG. 1:

[0113] 1: pipe 101 at the inlet to the pre-cooler 110;

[0114] 2: inlet pipe to the cooler 120;

[0115] 3: inlet pipe 125 to the dehydrator 130;

[0116] 4: outlet pipe 135 from the dehydrator 130;

[0117] 5: non-condensable gas transfer pipe at the inlet to the heat exchanger 134;

[0118] 6: non-condensable gas transfer pipe at the inlet to the heat exchanger 112;

[0119] 7: non-condensable gas removal pipe at the outlet 114 from the heat exchanger 112.

TABLE 4

	1	2	3	4	5	6	7
Temperature (° C.)	40	24	1	-75	-90	-40	30
Pressure	1	1	1	1	1	1	1
Nitrogen (t/h)	4432	4432	4432	4432	4432	4432	4432
Oxygen (t/h)	9189	9189	9189	9189	9189	9189	9189
Argon (t/h)	75	75	75	75	75	75	75
CO ₂ (t/h)	320	320	320	320	0	0	0
Water (t/h)	233	233	23	2	0	0	0

[0120] The cooling power needed for cooling the flue-gas from -75°C. to -90°C. and for CO_2 anti-sublimation (going from the vapor state at atmospheric pressure and -75°C. , to the liquid state at the triple point) is 50 MW (comprising 21 MW for cooling the flue-gas from -75°C. to -90°C. , and 29 MW for CO_2 anti-sublimation). On the basis of a nitrogen loop at 25 bar (-155°C. on the liquid side and 30°C. on the gas side), the pipe diameter will be 0.20 m for the pipe **43** situated on the liquid side if the flow speed of the liquid is 10 m/s (or 0.30 m if the flow speed of the liquid is 3 m/s), and the diameter will be 0.80 m for the pipe **44** on the gas side (10 m/s) (FIG. 3).

[0121] The dimensions of such a nitrogen cooling loop are thus entirely acceptable for easy practical implementation.

1. A method of capturing the carbon dioxide present in flue-gas, the method comprising the following steps:

- a) first cooling of the flue-gas in order to eliminate a fraction of the water present therein by condensation;
- b) dehydrating the flue-gas in order to eliminate the residual water;
- c) second cooling of the flue-gas by heat exchange so as to bring them to a temperature such that carbon dioxide passes directly from the gaseous state to the solid state by anti-sublimation;
- d) after removing the flue-gas, heating the solidified carbon dioxide in a closed enclosure up to the triple point where a liquid phase appears; and
- e) drawing off or pumping out the liquid and/or gaseous carbon dioxide to a thermally insulated tank;

the method being characterized in that a fraction of the recovered liquid carbon dioxide is recycled, and after expanding to atmospheric pressure, is reinjected during the second cooling step in continuous or intermittent manner in order to be mixed with the flue-gas previously delivered by the dehydration step.

2. A method according to claim **1**, characterized in that the fraction of the recovered liquid carbon dioxide that is recycled is reinjected during the second cooling step in the form of fine solid particles.

3. A method according to claim **1**, characterized in that the fraction of the recovered liquid carbon dioxide that is recycled is injected during the second cooling step into the inside of a heat exchanger.

4. A method according to claim **1**, characterized in that it further comprises a step of pre-cooling the flue-gas prior to said first cooling step, the pre-cooling step being performed by exchanging heat with at least one of the fluids comprising the liquid water recovered during the first cooling step and the flue-gas dehydration step, and the non-condensable compounds from the flue-gas that are recovered after said second cooling step.

5. A method according to claim **1**, characterized in that the first cooling of the flue-gas, the dehydration of the flue-gas, and the second cooling of the flue-gas make use of heat exchange with the flue-gas via cooling loops operating by heat exchange with the liquefied natural gas that is present in a methane terminal for regassification, and that is used as a cold source.

6. A method according to claim **5**, characterized in that the first cooling of the flue-gas and the dehydration of the flue-gas are performed by exchanging heat with the flue-gas via at least one cooling loop making use of glycol-containing water.

7. A method according to claim **5**, characterized in that the second cooling of flue-gas makes use of heat exchange with the flue-gas via at least one cooling loop making use of methane or of nitrogen.

8. A method according to claim **7**, characterized in that the second cooling of flue-gas makes use of heat exchange with the flue-gas via at least one additional cooling loop making use of ethylene or ethane.

9. A method according to claim **1**, characterized in that the dehydration of flue-gas includes a step of exchanging heat with the non-condensable compounds from the flue-gas recovered after the second cooling step.

10. A method according to claim **1**, characterized in that the step of dehydrating the flue-gas is performed discontinuously with alternation between a step of cooling the flue-gas to solidify water on the walls of a heat exchanger and a step of heating the solidified water in order to enable it to be recovered in liquid form.

11. A method according to claim **10**, characterized in that the solidified water is heated by exchanging heat with the flue-gas prior to the flue-gas being cooled during the step of cooling flue-gas with water being solidified.

12. A method according to claim **1**, characterized in that the second flue-gas cooling step for causing anti-sublimation of the carbon dioxide, and the solidified carbon dioxide heating step are performed discontinuously and in alternation.

13. A method according to claim **12**, characterized in that the step of heating the solidified carbon dioxide to the triple point at which a liquid phase appears is performed by heat exchange with the flue-gas prior to the flue-gas being cooled during the second cooling step.

14. A method according to claim **1**, characterized in that it further includes a step of recovering sulfur oxides contained in the flue-gas by anti-sublimation and reheating to the triple point where a liquid phase of sulfur oxides appears.

15. A system for capturing carbon dioxide present in flue-gas, the system comprising:

- a) first cooler means for cooling flue-gas and comprising at least one heat exchanger for eliminating a fraction of the water present in the flue-gas by condensation;
- b) flue-gas dehydration means;
- c) second cooler means for cooling flue-gas and comprising at least one heat exchanger for bringing the flue-gas to a temperature that causes anti-sublimation of the carbon dioxide present in the flue-gas;
- d) heater means for heating the solidified carbon dioxide in a closed enclosure in order to cause it to melt; and
- e) means for drawing off or pumping the liquid and/or gaseous carbon dioxide to a thermally insulated tank;

the system being characterized in that it further comprises expander means for expanding a fraction of the recovered liquid carbon dioxide to atmospheric pressure and for reinjecting said fraction of the carbon dioxide into the flue-gas at said second flue-gas cooler means.

16. A system according to claim **15**, characterized in that it includes means for reinjecting said recovered fraction of the liquid carbon dioxide in the form of fine solid particles into the flue-gas.

17. A system according to claim **15**, characterized in that the first cooler means comprise a heat exchanger between the flue-gas and at least one of the fluids comprising the liquid water recovered in the first cooler means or in the flue-gas dehydration means, and the non-condensable compounds of the flue-gas recovered at the inlet to the second cooler means.

18. A system according to claim **15**, characterized in that it includes cooling loops using heat-transferring fluids flowing firstly in heat exchangers present in a methane terminal for exchanging heat with the liquefied natural gas subjected to a regassification process, and secondly in heat exchangers placed in at least one of the first cooler means, the dehydration means, and the second cooler means in order to exchange heat with the flue-gas, giving rise to capture of carbon dioxide.

19. A system according to claim **18**, characterized in that it includes at least one cooling loop using glycol-containing water as its heat-transferring fluid and including at least one heat exchanger disposed in the first cooler means to the dehydration means.

20. A system according to claim **18**, characterized in that it includes at least one cooling loop using methane or nitrogen as its heat-transferring fluid and including at least one heat exchanger disposed in the second cooler means.

21. A system according to claim **20**, characterized in that it further includes at least one cooling loop using ethylene or ethane as its heat-transferring fluid and including at least one heat exchanger disposed in the second cooler means.

22. A system according to claim **15**, characterized in that it includes means for recovering non-condensable compounds from the flue-gas at the outlet from the second cooler means, and means for exchanging heat with at least one of the flue-gas dehydration means.

23. A system according to claim **15**, characterized in that the flue-gas dehydration means comprise at least first and second enclosures provided with heat exchangers and capable of receiving flue-gas discontinuously so that each of them can act in turn to cool flue-gas and solidify the water contained therein on the walls of the corresponding enclosure, and to heat the solidified water in order to enable it to be recovered in liquid form.

24. A system according to claim **15**, characterized in that the second flue-gas cooler means and said heater means comprise at least first and second enclosures provided with heat exchangers and capable of receiving flue-gas discontinuously in such a manner that each of them in turn cools flue-gas with anti-sublimation of the carbon dioxide that is deposited on the walls of the corresponding enclosure, and heats the solidified carbon dioxide in order to cause it to melt.

25. A system according to claim **15**, characterized in that it further comprises means for recovering sulfur oxides from said heater means in a closed enclosure.

26. A method according to claim **2**, characterized in that the fraction of the recovered liquid carbon dioxide that is recycled is injected during the second cooling step into the inside of a heat exchanger;

it further comprises a step of pre-cooling the flue-gas prior to said first cooling step, the pre-cooling step being performed by exchanging heat with at least one of the fluids comprising the liquid water recovered during the first cooling step and the flue-gas dehydration step, and the non-condensable compounds from the flue-gas that are recovered after said second cooling step;

the first cooling of the flue-gas, the dehydration of the flue-gas, and the second cooling of the flue-gas make use of heat exchange with the flue-gas via cooling loops operating by heat exchange with the liquefied natural gas that is present in a methane terminal for regassification, and that is used as a cold source;

the first cooling of the flue-gas and the dehydration of the flue-gas are performed by exchanging heat with the flue-gas via at least one cooling loop making use of glycol-containing water;

the second cooling of flue-gas makes use of heat exchange with the flue-gas via at least one cooling loop making use of methane or of nitrogen;

the second cooling of flue-gas makes use of heat exchange with the flue-gas via at least one additional cooling loop making use of ethylene or ethane;

the dehydration of flue-gas includes a step of exchanging heat with the non-condensable compounds from the flue-gas recovered after the second cooling step;

the step of dehydrating the flue-gas is performed discontinuously with alternation between a step of cooling the flue-gas to solidify water on the walls of a heat exchanger and a step of heating the solidified water in order to enable it to be recovered in liquid form;

the solidified water is heated by exchanging heat with the flue-gas prior to the flue-gas being cooled during the step of cooling flue-gas with water being solidified;

the second flue-gas cooling step for causing anti-sublimation of the carbon dioxide, and the solidified carbon dioxide heating step are performed discontinuously and in alternation;

the step of heating the solidified carbon dioxide to the triple point at which a liquid phase appears is performed by heat exchange with the flue-gas prior to the flue-gas being cooled during the second cooling step; and

it further includes a step of recovering sulfur oxides contained in the flue-gas by anti-sublimation and reheating to the triple point where a liquid phase of sulfur oxides appears.

27. A system according to claim **16**, characterized in that the first cooler means comprise a heat exchanger between the flue-gas and at least one of the fluids comprising the liquid water recovered in the first cooler means or in the flue-gas dehydration means, and the non-condensable compounds of the flue-gas recovered at the inlet to the second cooler means;

it includes cooling loops using heat-transferring fluids flowing firstly in heat exchangers present in a methane terminal for exchanging heat with the liquefied natural gas subjected to a regassification process, and secondly in heat exchangers placed in at least one of the first cooler means, the dehydration means, and the second cooler means in order to exchange heat with the flue-gas, giving rise to capture of carbon dioxide;

it includes at least one cooling loop using glycol-containing water as its heat-transferring fluid and including at least one heat exchanger disposed in the first cooler means to the dehydration means;

it includes at least one cooling loop using methane or nitrogen as its heat-transferring fluid and including at least one heat exchanger disposed in the second cooler means;

it further includes at least one cooling loop using ethylene or ethane as its heat-transferring fluid and including at least one heat exchanger disposed in the second cooler means;

it includes means for recovering non-condensable compounds from the flue-gas at the outlet from the second cooler means, and means for exchanging heat with at least one of the flue-gas dehydration means;

the flue-gas dehydration means comprise at least first and second enclosures provided with heat exchangers and capable of receiving flue-gas discontinuously so that each of them can act in turn to cool flue-gas and solidify the water contained therein on the walls of the corresponding enclosure, and to heat the solidified water in order to enable it to be recovered in liquid form;
the second flue-gas cooler means and said heater means comprise at least first and second enclosures provided with heat exchangers and capable of receiving flue-gas

discontinuously in such a manner that each of them in turn cools flue-gas with anti-sublimation of the carbon dioxide that is deposited on the walls of the corresponding enclosure, and heats the solidified carbon dioxide in order to cause it to melt; and
it further comprises means for recovering sulfur oxides from said heater means in a closed enclosure.

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