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INSTALLATION FOR CRYOGENIC
ADSORPTION AND SEPARATION FOR
PRODUCING CO₂**Aug. 8, 2005 (FR) 0552459
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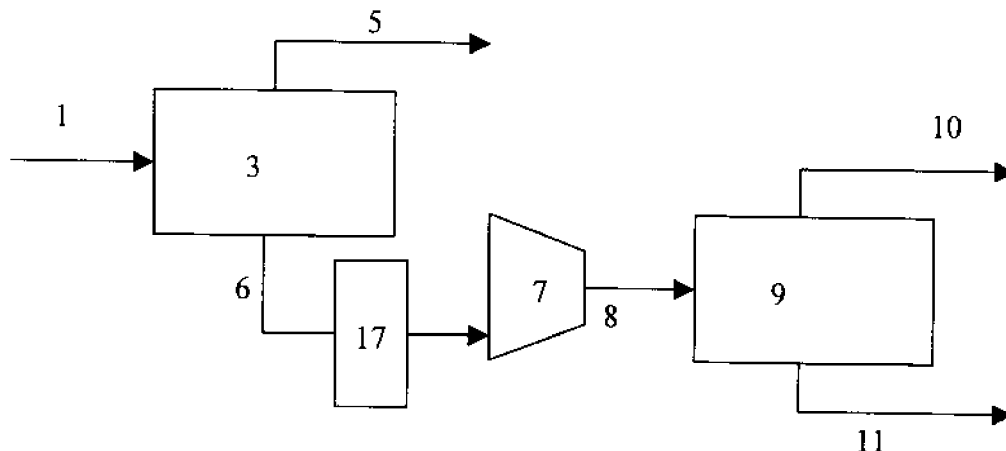
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(57) **ABSTRACT**

An integrated process and installation implementing a unit of adsorption (3) and a cryogenic unit (9), in which a gas of food containing of CO₂ is sent to the unit of adsorption (3) where it separates in a first flow enriched out of CO₂ (6) and a first flow impoverished of CO₂ (5), first flow enriched out of CO₂ being sent to the cryogenic unit (9) where it is separate in a second flow rich in CO₂ (11) and a second flow low in CO₂ (10). The first flow enriched out of CO₂ (6) resulting from the unit from adsorption (3) is sent towards means of homogenization (17), a such storage capacity or analogue, making it possible to attenuate the cyclic variations of flow, composition and/or gas pressure, then subjected to at least a stage of intermediate compression (7) before its entry in the cryogenic unit (9). The first gas enriched out of CO₂ (6) outgoing by the unit by adsorption (3) contains between 40 and 95% of CO₂, preferentially between 60 and 85% of CO₂.



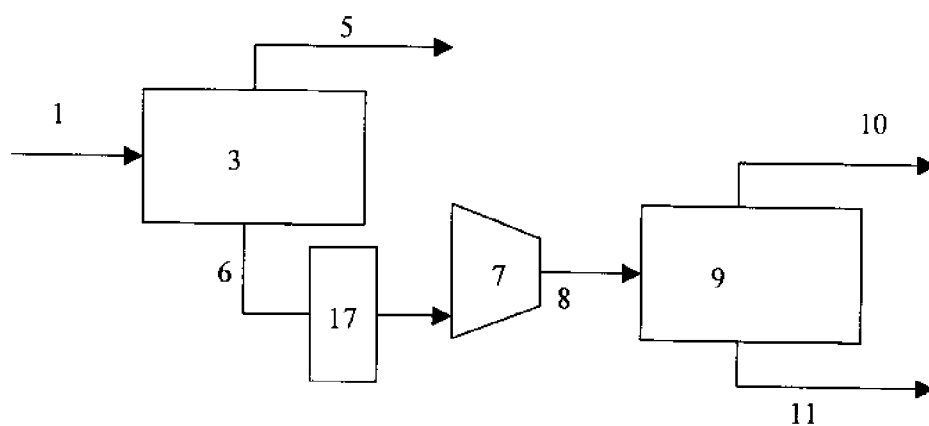


Fig. 1

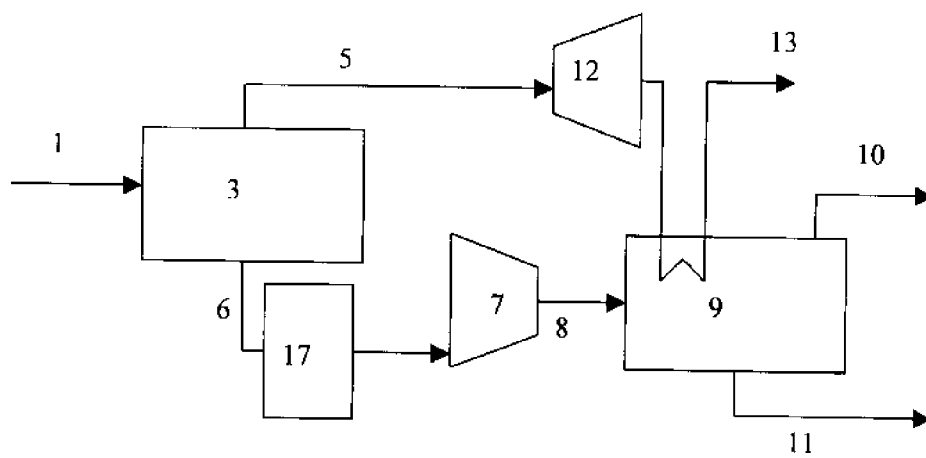


Fig. 2

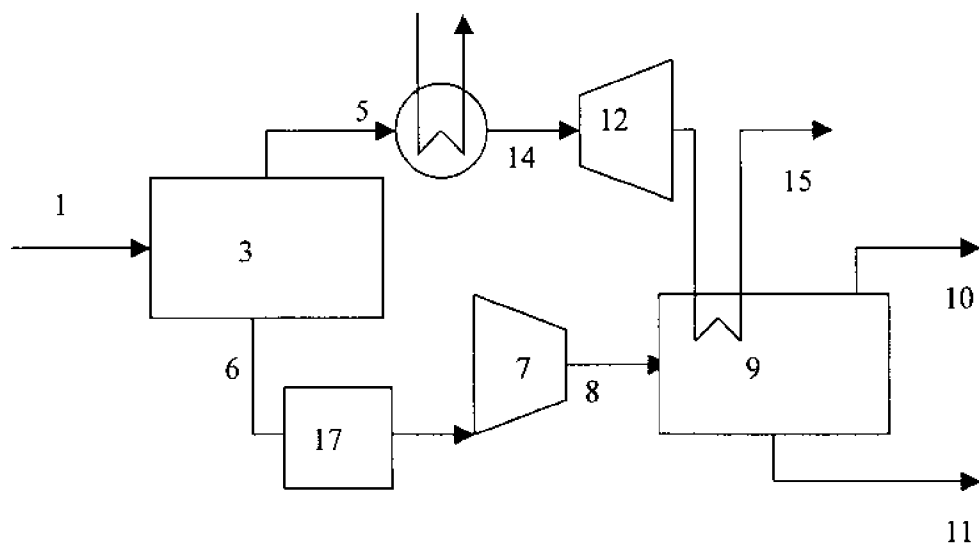


Fig. 3

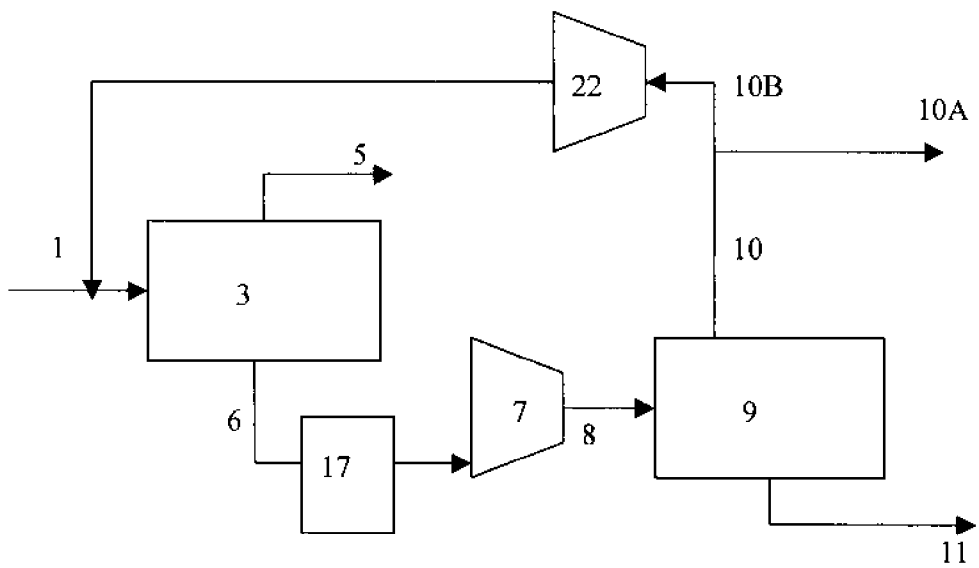


Fig. 4

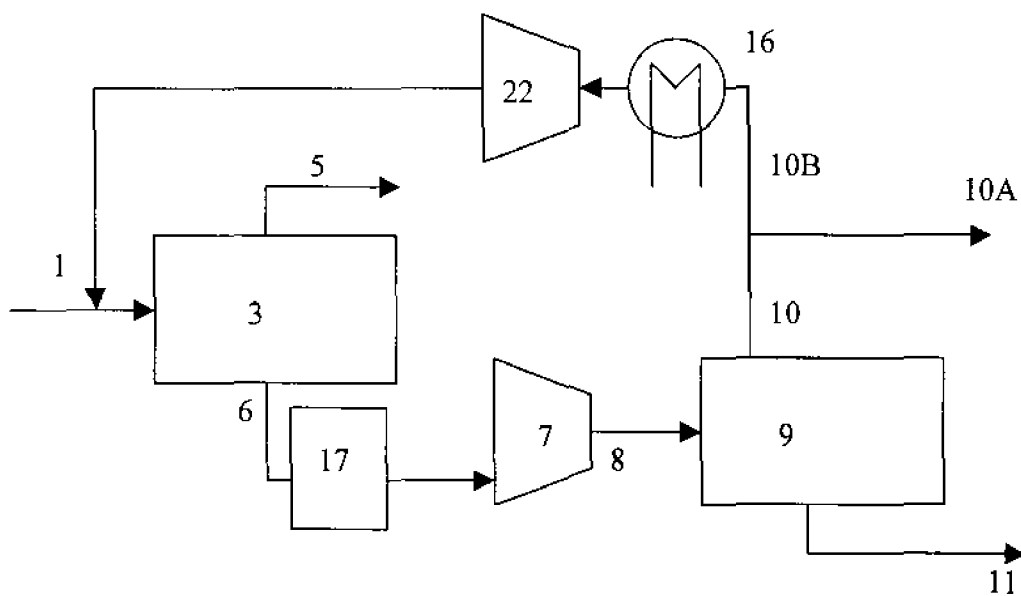


Fig. 5

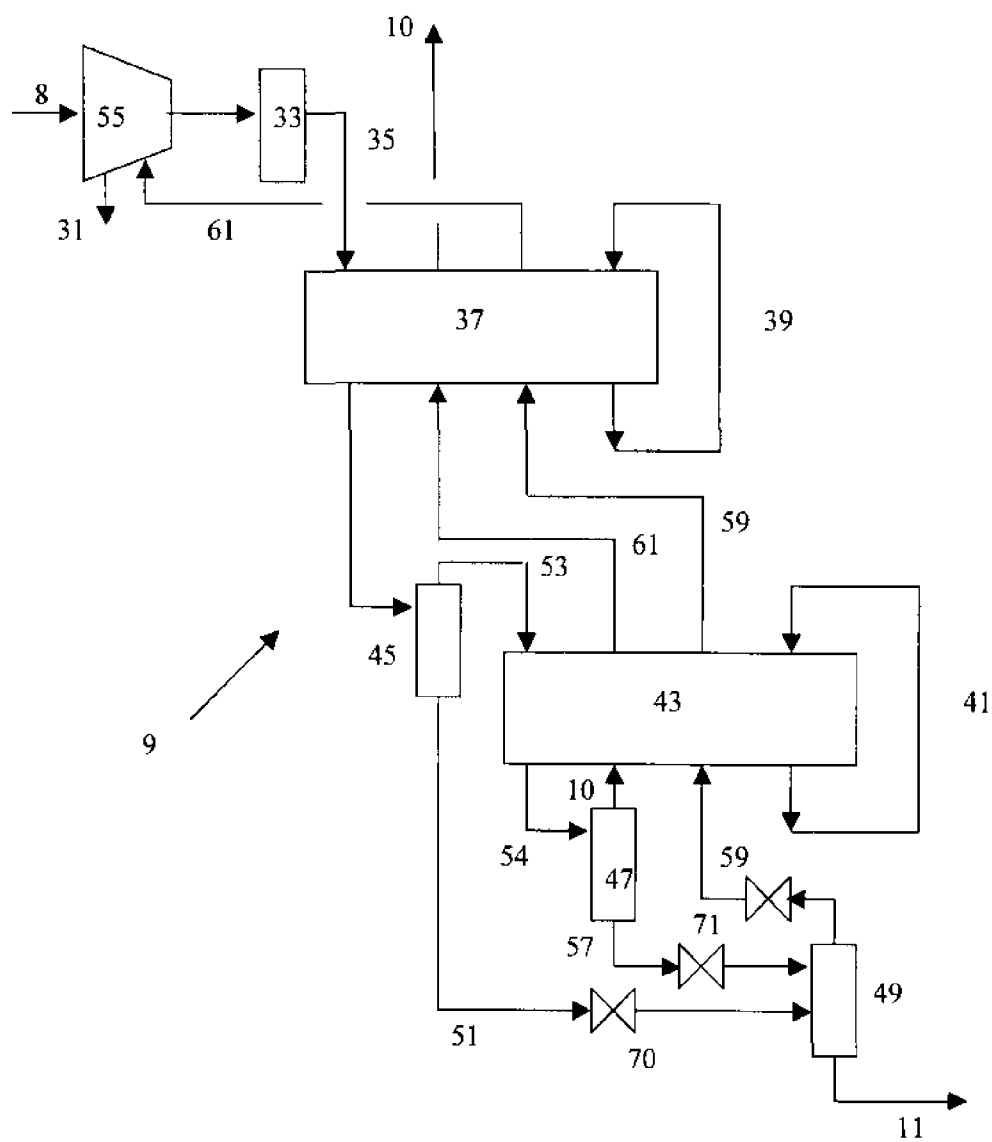


Fig. 6

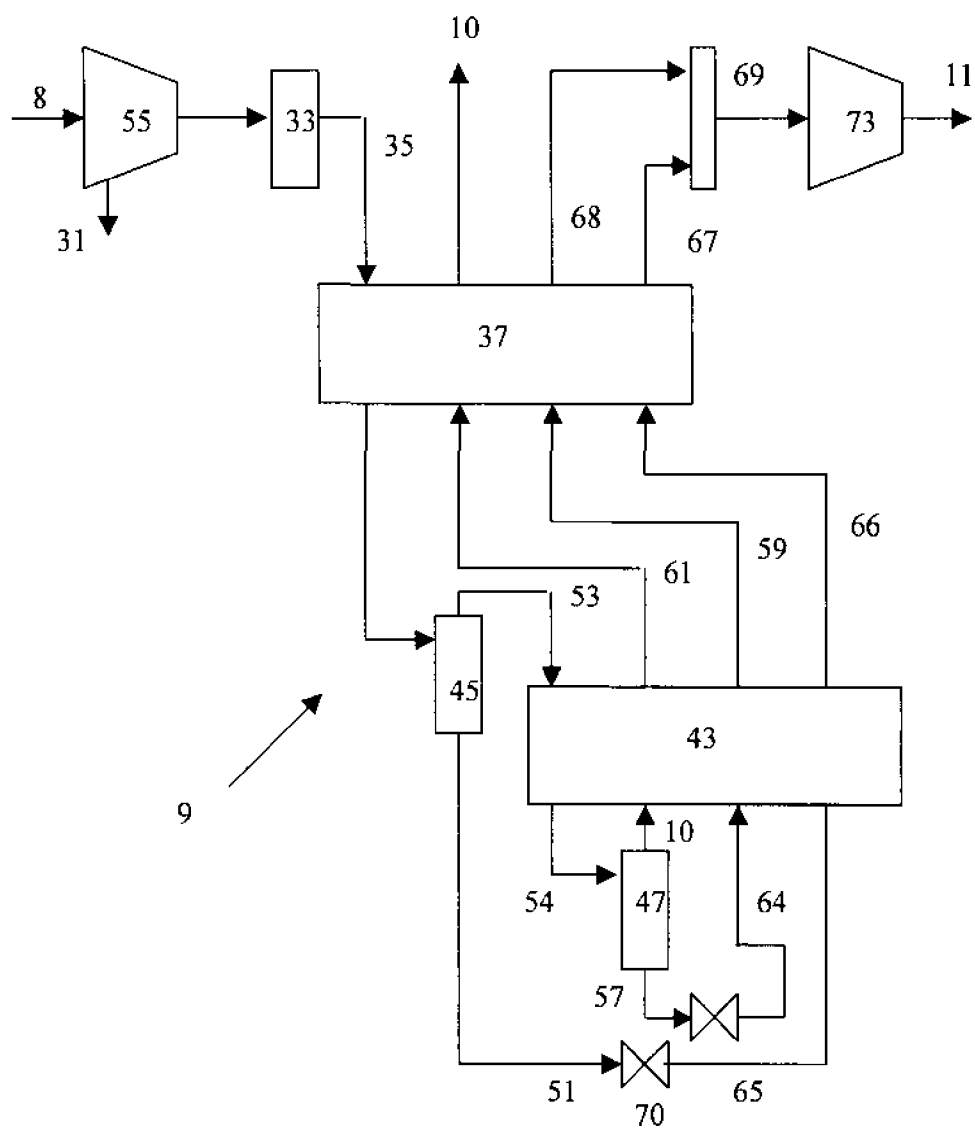


Fig. 7

INTEGRATED METHOD AND INSTALLATION FOR CRYOGENIC ADSORPTION AND SEPARATION FOR PRODUCING CO₂

[0001] The present invention relates to an integrated method of adsorption and cryogenic separation for separating CO₂ contained in a gas and to an installation for implementing such a method.

[0002] The recovery of CO₂ from gases or flue gases is spreading inexorably due to the systems installed for limiting greenhouse gas emissions.

[0003] The prevalent technology for removing and/or recovering the CO₂ contained in industrial effluents is chemical absorption and, more particularly, scrubbing with amines (MDEA, MEA, etc.) which serve to produce pure low pressure CO₂, typically having a CO₂ purity above 99%.

[0004] However, the chemical scrubbing methods have many limitations or drawbacks, that is: large quantity of steam required, sensitivity to oxygen, corrosion, high operating cost, solvent entrainment and, in general, releases of chemicals in non-negligible quantities, such as amines, ammonia, salts issuing from the amine regenerator, amine degeneration products, etc.

[0005] Another technology available for recovering the CO₂, not having these drawbacks, and in particular, not requiring large quantities of steam, is pressure swing adsorption, like the VPSA (Vacuum Pressure Swing Adsorption), VSA (Vacuum Swing Adsorption) or PSA (Pressure Swing Adsorption) methods.

[0006] In the context of the invention, the acronyms have the following meanings:

[0007] VPSA unit: a gas separation or purification unit using a cyclic adsorption method comprising at least one adsorption phase on an adsorbent at a pressure above 1.5 bar absolute, and a regeneration phase during which the pressure is lower than atmospheric pressure.

[0008] VSA unit: a gas separation or purification unit using a cyclic method comprising at least one adsorption phase on an adsorbent solid at a pressure lower than 1.5 bar absolute, and a regeneration phase during which the pressure is lower than atmospheric pressure.

[0009] PSA unit: a gas separation or purification unit using a cyclic method comprising at least one adsorption phase on an adsorbent solid at a pressure above 1.5 bar absolute, and a regeneration phase during which the pressure is equal to or higher than atmospheric pressure.

[0010] The VPSA, VSA and PSA units will be referred to below by the generic term "adsorption units".

[0011] Furthermore, in the context of the invention:

[0012] all the gas compositions are expressed on a dry basis. The basic dry composition of the component is the ratio, by mass or by volume, of the quantity of material of this component to the total quantity of material present, not including water molecules. Thus, if a stream containing, for example, 70% CO₂ also contains 10% water, the basic dry CO₂ content of the stream is about 78% (70%/90%);

[0013] all the gas compositions are stated in percentages by volume;

[0014] the relative humidity of a gas is the ratio, in percentage, of the partial pressure of the water vapor effectively

contained in the gas to the water vapor saturation pressure under the same pressure and temperature conditions, according to the usual definition;

[0015] the gas compositions issuing from the adsorption methods described in this document are mean compositions, averaged over a whole number of method cycles, the adsorption methods being cyclic methods;

[0016] the recovery yield of a compound of a separation unit is the ratio between the quantity of this compound entering the unit and the quantity of this compound leaving the unit in the desired product form.

[0017] Today, the adsorption method is used in the iron and steel industry for deballasting gases issuing from processes of the DRI (Direct Reduced Iron) or COREX type. In this case, the purge gas from the adsorption method, which is CO₂ rich, that is, typically containing between 60 and 80% CO₂, 25% CO and 5% N₂, leaving this unit, is used as fuel gas because it still contains a significant quantity of CO. The flue gases issuing from the combustion of this gas are discharged to the atmosphere. The streams from a DRI unit are preferably decarbonated by a VPSA unit, as described in document U.S. Pat. No. 5,858,057 and U.S. Pat. No. 5,676,732. However, the drawback of the flowcharts described in these documents is that the CO₂ obtained is not utilized or stored but is simply discharged to the atmosphere.

[0018] Furthermore, to improve the operation of a VPSA CO₂ method, documents U.S. Pat. No. 5,582,029 and U.S. Pat. No. 6,562,103 teach the use of an external purge gas, poor in CO₂, to elute the adsorbent bed, for example, nitrogen produced by an air separation unit, or a natural gas stream. However, the drawback here is that the CO₂ leaving the purge is diluted in these purge gases and therefore cannot be utilized or stored.

[0019] An adsorption unit is incapable of producing, on an economically acceptable basis or industrially, CO₂ in a purity higher than 90%, in particular a purity between 90 and 96%, and hence particularly even less in a purity higher than 96%, from a CO₂ poor feed gas, that is, often containing less than 45% CO₂.

[0020] Because of this, these methods, used alone, are not suitable for concentrating CO₂ for its industrial utilization, re-injection and its storage in geological formations (EOR, ECBM, etc.) or for any other use of CO₂ requiring CO₂ purities higher than 90%.

[0021] For their part, the cryogenic CO₂ separation units, including liquefiers, are only used to process gases having a concentration above 50%, preferably above 70% and generally above 90%, because the CO₂ recovery yield of these units declines sharply when the proportion of gas other than CO₂ increases, due to the physical properties of CO₂ mixtures with nitrogen, carbon monoxide, hydrogen, oxygen, methane, etc., and the triple point of CO₂, which prevents falling to temperatures below -50° C.

[0022] In the context of the invention, "cryogenic unit" means an industrial unit for cooling a fluid, for example CO₂, in which at least one process fluid is cooled to a temperature lower than or equal to 0° C. and undergoes at least one partial condensation step. This unit may, for example, produce CO₂ in gas, liquid or supercritical form. A unit producing a liquid as a product is called a liquefier.

[0023] The recovery of CO₂ from the offgas of an H₂ PSA by a cryogenic unit is described in US-A-2002/0073845 and WO-A-9935455. The H₂ PSA offgas typically contains about 50% CO₂. These patents describe an original cryogenic

method for recovering CO₂ from this offgas but do not describe the optimized integration of the H₂ PSA and the cryogenic unit, and in particular, do not explain how the interface between the PSA, which is a batch and cyclic process, and the cryogenic unit, which is a continuous process, is implemented. Furthermore, the CO₂ content at the inlet of the cryogenic unit is imposed by the hydrogen production performance of the PSA, but there is no integration between the two units and no combined optimal operation. For example, no recycling between the two units is considered.

[0024] Document EP-A-341879 also describes a method for coproducing CO₂ and H₂, in which a syngas issuing from an SMR followed by a shift reactor is sent to an H₂ PSA from which the offgas, which contains about 50% CO₂, is sent to a CO₂ PSA. This CO₂ PSA produces a second CO₂ enriched gas containing at least 98% CO₂, which is sent to a cryogenic separation apparatus that produces a liquid containing at least 99.9% CO₂. In this patent, the CO₂ PSA produces a CO₂ in a high purity (>98%), which culminates in an overall CO₂ recovery method that is underoptimized. Moreover, although the interface between the H₂ PSA and the CO₂ PSA is described, the interface between the CO₂ PSA and the liquefier is not addressed, although it is a point that raises important problems between a cyclic process and a continuous process.

[0025] The coupling of a PSA with a liquefaction unit is also described in Takamura et al., *The Canadian Journal of Chemical Engineering*, 79 (5), 812-816: Application of high pressure swing adsorption process for improvement of CO₂ recovery system from flue gas; 2001. An ultra cold separator is placed on the offgas from a PSA processing the effluents from a boiler. The incondensable compounds from the liquefier are introduced into a "high pressure" PSA and the purge from this PSA is reintroduced to the feed of the liquefier to improve the yield thereof. However, there is no mention of the way in which the cyclic PSA is coupled with the continuous liquefier.

[0026] Document EP-B-0417922 describes a method for producing CO₂ from a gas that is relatively poor in CO₂, which is first sent to adsorption drying beds and then to a distillation column. The incondensable compounds from the column are then sent to a PSA unit and the CO₂ rich gas issuing from this PSA is recycled to the inlet of the liquefier. By the same principle, document GB-A-2174379 describes the use of a membrane instead of the PSA to separate the CO₂ from the stream of incondensables issuing from the column. These flowcharts, in which the first CO₂ separation takes place by cryogenic distillation, can only be economically viable if the CO₂ content of the feed gas is not too low, typically if it is higher than about 50%.

[0027] Document EP-A-1319911 describes a CO₂ liquefaction method in which drying by adsorption precedes the cryogenic separation of the CO₂. This document does not describe a pre-separation of the CO₂ by adsorption unit.

[0028] Document EP-A-0945163 describes the combined use of membrane modules and PSA to separate and purify hydrogen. This system is not optimized for recovering CO₂ and, more precisely, does not comprise a cryogenic portion that would serve to meet the more stringent specifications on the CO₂ produced.

[0029] Furthermore, documents U.S. Pat. No. 4,639,257 and U.S. Pat. No. 4,602,477 teach methods using a combination of a membrane and a cryogenic distillation unit to sep-

arate the CO₂. The adsorption units employed only serve to remove the water from the gas stream and not to separate the CO₂ significantly.

[0030] It is a particular object of the present invention to overcome the drawbacks of the prior art and to propose solutions for implementing and optimizing a method integrating an adsorption unit and a cryogenic unit for the effective separation of CO₂ from a stream containing less than 60% CO₂, the other components being more volatile components, for example CO, N₂, H₂, CH₄, etc.

[0031] More precisely, one object of the inventive method is to obtain, at minimum cost, a CO₂ recovery yield of about 90% and/or a CO₂ product purity meeting the specifications for geological disposal (aquifers, coal 30 seams, etc.) and/or the enhanced recovery of fossil fuels (EOR, ECBM, etc.). For example, the CO₂ purities desired for these applications are generally above about 89%, typically above 94%, and lower than about 99%. **35** One of the subjects of the invention is accordingly an integrated method using an adsorption unit coupled to a cryogenic unit, in which a feed gas containing CO₂ is sent to the adsorption unit where it is separated into a first CO₂ enriched stream and a first CO₂ depleted stream, the first CO₂ enriched stream being sent to the cryogenic unit where it is separated into a second CO₂ rich stream and a second CO₂ depleted stream, characterized in that the first CO₂ enriched stream issuing from the adsorption unit is first sent to gas homogenizing means for attenuating the cyclic variations of flow rates, pressure and/or composition of this first stream, inherent in the cyclic character of the adsorption unit, and then subjected to at least one intermediate compression step before entering the cryogenic unit, that is, upstream and/or prior to its entry into the cryogenic unit.

[0032] The gas homogenizing means for attenuating the cyclic variations of the stream issuing from the adsorption unit may be, for example, an intermediate storage unit, such as a vessel or reservoir, optionally maintained at a substantially constant pressure. More precisely, this intermediate gas storage unit may, for example, be a gas holder having a variable volume and at substantially constant pressure, or a vessel having a fixed volume equipped with a pressure control system for maintaining a substantially constant pressure.

[0033] In other words, one of the aspects of the present invention is the coupling of an adsorption unit and a cryogenic unit using a first gas homogenizing step for attenuating the cyclic variations of flow rates, compositions and/or pressures of the first CO₂ enriched stream issuing from the adsorption unit and a second intermediate compression step, these two steps being carried out between the adsorption separation step and the cryogenic separation step, that is between the adsorption unit and the cryogenic unit.

[0034] The homogenizing step serves to attenuate the cyclic variations of the stream issuing from the adsorption unit and can be carried out by using an intermediate gas storage unit or any other device suitable for performing this attenuation/homogenization function, and suitable for collecting all or part of the CO₂ enriched stream leaving the adsorption unit.

[0035] The adsorption unit therefore first carries out a "pre-separation" of the CO₂ and the cryogenic unit then carries out the final separation of the CO₂ by means of various integration devices installed between the adsorption unit and the cryogenic unit.

[0036] The use of gas homogenizing means or a device for attenuating the cyclic variations of the CO₂ enriched stream

issuing from the adsorption unit (flow rate, composition, pressure, etc.) inherent in the cyclic operation of the adsorption unit, serves to ensure continuous operation of the compressor and of the cryogenic unit located downstream.

[0037] A system is thereby obtained coupling a cyclic batch process employed by the adsorption unit, and a continuous system employed by the cryogenic unit, with reduced process control means at the interface.

[0038] Furthermore, in case of interruption of one of these two units, for maintenance for example, the two units can be easily uncoupled.

[0039] Moreover, the fact of carrying out a compression up to at least 15 bar upstream of the cryogenic unit serves to guarantee the desired yields in the cryogenic unit on input gases containing between 40% and 95% CO₂, thereby relaxing the constraints on the separation performance of the adsorption unit.

[0040] Symmetrically, part of the incondensable gases issuing from the cryogenic unit is optionally recycled to the adsorption unit and therefore serves to relax the constraints on the separation performance of the cryogenic unit.

[0041] An integrated and combined system is thereby obtained between the adsorption unit and the cryogenic unit, which serves to optimize the separation costs of the overall system.

[0042] Depending on the case, the inventive method may further comprise one or more of the following features:

[0043] the first CO₂ enriched stream issuing from the adsorption unit has a pressure of less than 4 bar, preferably less than 2 bar, and a CO₂ content of between 40% and 95%, preferably between 60% and 85% and/or a relative humidity above 5%,

[0044] the second CO₂ rich stream issuing from the cryogenic separation unit has a CO₂ content above 80%, preferably above 90%, and even more preferably above 95%.

[0045] the first CO₂ enriched gas leaving the adsorption unit is sent to the gas homogenizing means for attenuating the cyclic variations in flow rate, composition and/or pressure of this gas, and is then subjected to the intermediate compression,

[0046] the gas homogenizing means is a mixing vessel or reservoir, for example a constant volume vessel with pressure control or a gas holder having a variable volume and substantially constant pressure,

[0047] the first CO₂ depleted stream produced by the adsorption unit is expanded in a turbine which can provide refrigerating capacity to the cryogenic unit,

[0048] the first CO₂ poor gas produced by the adsorption unit is first cooled before being expanded in the turbine,

[0049] at least part of the second CO₂ poor gas leaving the cryogenic unit is returned to the adsorption unit, particularly either to the suction inlet of the compressor feeding the adsorption unit, or upstream of the adsorber(s) of the adsorption unit, or in the adsorbers during a repressurizing step, in cocurrent or countercurrent, or in the adsorber(s) during an adsorption step,

[0050] at least part of the second CO₂ depleted gas leaving the cryogenic unit is expanded in a turbine and then recycled to the adsorption unit, either to the suction inlet of the feed compressor, or upstream of the adsorber(s), or in the adsorber(s) during a repressurizing step, in cocurrent or countercurrent, or in the adsorber(s) during an adsorption step,

[0051] before entering the turbine, the recycled gas is first heated by direct combustion of this gas (injection of air or

enriched air) and/or by heating in a boiler preferably burning blast furnace gas and/or by exchange with a fluid from the steel plant, whose temperature is higher than 150° C. and/or by exchange with the first CO₂ enriched gas produced by the adsorption unit upstream of the cryogenic unit,

[0052] at least part of the second CO₂ poor gas leaving the cryogenic unit is used as fuel for heating the gas of the cryogenic unit, heating the regeneration heater of the cryogenic unit, for example drying by adsorption, and/or heating the first CO₂ poor gas from the adsorption unit, before or after expansion in an optional turbine, and/or heating a regeneration heater of an air separation unit and/or producing steam which can be used in the installation by the regeneration heater of the cryogenic unit and/or, one or more drive turbines of the machines and/or a refrigerating unit by absorption serving for example to cool the gas before the purifiers of the cryogenic unit and/or a heat exchanger heating the first CO₂ poor gas leaving the adsorption unit,

[0053] at least part of the first CO₂ poor gas leaving the adsorption unit is used as fuel to heat the regeneration heater, for example for drying beds, of the cryogenic unit and/or to produce steam which can be used in the installation by the regeneration heater and/or one or more drive turbines of the machines and/or a refrigerating unit by absorption serving for example to cool the gas before the purifiers of the cryogenic unit and/or a heat exchanger heating the first CO₂ poor gas leaving the adsorption unit,

[0054] the refrigerating unit of the cryogenic unit also serves to cool the gas entering the adsorption unit,

[0055] the first CO₂ enriched gas leaving the adsorption unit is sent to a mixing vessel or reservoir before being introduced into the cryogenic unit,

[0056] the incondensable compounds leaving the cryogenic unit are sufficiently cooled to freeze CO₂ in the form of dry ice and to separate the CO₂ thereby frozen from the stream containing the incondensable compounds,

[0057] at least part of the CO₂ enriched stream compressed in the intermediate compression step is cooled to a temperature above 0° C., and the liquid part which condenses is preferably removed, for example in a phase separation device.

[0058] According to another aspect, the invention also relates to an integrated installation for producing CO₂ from a feed gas containing CO₂, comprising an adsorption unit for separating the gas containing CO₂ into a first CO₂ enriched stream and a first CO₂ depleted stream, the adsorption unit feeding a cryogenic unit with said first CO₂ enriched stream, and a cryogenic unit for separating the first CO₂ rich stream issuing from the adsorption unit into a second CO₂ rich stream and a second CO₂ poor stream, characterized in that the CO₂ enriched stream issuing from the adsorption unit has a CO₂ content of between 40 and 95% and in that it further comprises a gas homogenizing device or means suitable for attenuating the cyclic variations (flow rate, composition, pressure, etc.) of the CO₂ enriched stream issuing from the adsorption unit and intermediate compression means, arranged on the path of the first CO₂ enriched stream, between the adsorption unit and the cryogenic unit. Advantageously, the CO₂ enriched stream issuing from the adsorption unit has a CO₂ content of between 60 and 85%.

[0059] Preferably, the gas homogenizing means are arranged upstream of the compression means, that is between the adsorption unit and the compression means.

[0060] The installation of the invention optionally also comprises means for carrying out gas recyclings between the adsorption unit and the cryogenic unit, for example means for recycling at least part of the incondensable gases issuing from the cryogenic unit to the adsorption unit, particularly either at the suction inlet of the compressor feeding the adsorption unit, or upstream of the adsorber(s) of the adsorption unit, or in the adsorbers during a repressurizing step, in cocurrent or countercurrent, or in the adsorber(s) during an adsorption step, the recycles optionally passing through heating, combustion and expansion means.

[0061] The invention is described in greater detail with reference to

[0062] FIGS. 1 to 5, which illustrate embodiments of the invention, and

[0063] FIGS. 6 and 7 which are diagrams of cryogenic units 9 suitable for being used in a method according to the invention.

[0064] FIG. 1 shows an adsorption unit 3 of the VPSA, VSA or PSA type fed with a feed gas 1, also called gas to be processed, which contains, for example between 10 and 60% CO₂, mixed with at least one other gas which may be N₂, CO, H₂, O₂, CH₄, Ar, H₂O, etc. This gas may, for example be a blast furnace gas containing on average for example 23% CO₂, 23% CO, 50% N₂ and 4% H₂, available at about 50° C. and 2 bar absolute, at a flow rate for example between 50 000 Nm³/h and 800 000 Nm³/h.

[0065] The gas 1 to be processed by the adsorption unit 3 is typically at a pressure between 1 and 10 bar absolute. This pressure is reached by optionally adding a compressor upstream of the adsorber(s) of the adsorption unit 3.

[0066] The method of the present invention is an integrated method using, in series, an adsorption unit 3 coupled with a cryogenic unit 9, the combination being optimized for producing CO₂ at minimum cost, with a CO₂ recovery yield of about 90% and/or a typical CO₂ product purity of about 90 to 99%, particularly by the passage of the CO₂ enriched gas issuing from the adsorption unit through a buffer vessel or reservoir 17 constituting all or part of the gas homogenizing means, and/or an intermediate compression, as described below.

[0067] According to the method shown in FIG. 1 appended hereto, the gas 1 to be processed is first sent to the adsorption unit 3 or to the adsorption units, in the case in which a plurality of adsorption units are employed, operating in parallel, where it is separated into a first CO₂ enriched stream 6 and a first CO₂ depleted stream 5.

[0068] The first CO₂ enriched stream 6 is produced at lower than 4 bar, typically at lower than 2 bar, for example between 1 and 2 bar, and is then sent to the cryogenic unit 9, without undergoing other separation steps, except optionally a recovery of part of the water it contains.

[0069] The first CO₂ enriched stream 6 leaving the adsorption unit 3 has a CO₂ content of between 40% and 95%, typically between 60% and 85%, a pressure of less than 4 bar, typically about 1 to 2 bar, and a relative humidity generally of at least 5%.

[0070] According to the invention, the step of attenuation of the cyclic variations in flow rate, composition, pressure, etc. 17 and the intermediate compression step 7 are carried out on the first CO₂ enriched stream 6 leaving the adsorption unit 3, upstream of the cryogenic unit 9, via one or more compressors or any other suitable gas compression device, placed between these two units 3, 9.

[0071] The gas homogenizing means or device for attenuating the cyclic variations 17, placed on the path of the CO₂ enriched stream leaving the adsorption unit 3, before its intermediate compression 7, is for example a constant volume vessel with pressure control or a gas holder having a variable volume and substantially constant pressure. The pressure of this mixing vessel or reservoir is typically lower than 4 bar absolute, preferably lower than 2 bar absolute. The intermediate compression step serves to raise the pressure of the CO₂ enriched gas issuing from the adsorption unit 3 and stored in the mixing vessel or reservoir 17 from a low pressure lower than 4 bar absolute to pressure levels compatible with an efficient cryogenic separation, that is to a pressure of above 15 bar, typically between 20 and 80 bar, in order to improve the CO₂ recovery yield in the cryogenic unit.

[0072] In the cryogenic unit 9, the compressed gas stream is separated into a second CO₂ rich stream 11 and a second CO₂ poor stream 10. The second CO₂ rich stream 11 leaving the cryogenic unit 9 has a CO₂ content above 80%, preferably at least 90% even more preferably at least 94%.

[0073] In other words, the first CO₂ enriched stream 6 leaving the adsorption unit 3 is then sent to the gas homogenizing means, then to one or more intermediate compression means or devices 7, such as one or more compressors or any other device suitable for carrying out a gas compression, before being conveyed, via the line 8, to a cryogenic unit 9 where it is condensed at least partially and at least once.

[0074] Before being partially condensed, the first CO₂ enriched stream 6 issuing from the adsorption unit is therefore compressed to a pressure above 6 bar absolute, preferably above 20 bar absolute, typically between 20 and 80 bar and preferably between 30 and 50 bar, for a mean CO₂ content of the stream 6 of 40 to 95%, typically between 60 and 85% at the outlet of the adsorption unit 3.

[0075] The cryogenic unit 9, which may, for example be a liquefier, produces a second CO₂ poor gas 10 and a second CO₂ rich gas 11 containing at least 80% CO₂ and preferably 90 to 99% CO₂, or optionally even more than 99% CO₂.

[0076] The CO₂ can then be stripped to produce a gas containing even purer CO₂, for example in a stripping column (not shown) located downstream, before being sent to a user or storage site.

[0077] Furthermore, the adsorption unit 3 further comprises one or more adsorbers operating in parallel, a system of valves and optionally one or more vacuum pumps in the case of a VPSA or VSA unit, a compressor of the gas to be processed, a CO₂ enriched gas storage vessel or reservoir, and/or a CO₂ depleted gas storage vessel or reservoir.

[0078] Moreover, the cryogenic unit 9 may in particular comprise one or more gas prepurifiers, typically containing alumina or a molecular sieve, an active carbon or a silica gel, and their regeneration heater, a cold heat exchanger and optionally one or more condensers/reboilers, separator pots, distillation columns, compressors, devices for the catalytic removal or not of the CO₂ and hydrogen, mechanical or absorption refrigerating unit, and/or precooling device before the dryers.

[0079] FIG. 2 differs from FIG. 1 only in that the first CO₂ depleted gas 5 is expanded in a turbine 12. The energy recovered on the turbine 12 can either serve to drive the compressor 7, even partially with an auxiliary motor, or can be used to generate electricity. The turbine 12 transfers part of its refrigerating capacity to the cryogenic unit 9, via the line 13.

[0080] FIG. 3 differs from FIG. 2 only in the incorporation of a cooler 14 upstream of the turbine 12, which serves to transfer additional refrigerating capacity to the cryogenic unit 9, by sending the gas expanded in the turbine 12 to a heat exchanger of the cryogenic unit 9. In the case in which the liquid CO₂ vaporizes in the cryogenic unit, most or even all of the refrigerating input issues from this latent heat. However, a contribution, even a small one, to offset the heat losses, may be necessary or desirable, and can accordingly be supplied by the expanded gas. On the contrary, if the purpose of the expansion is to produce energy rather than to supply refrigerating capacity to the cryogenic unit, it is then more advantageous to heat the stream to be expanded.

[0081] FIG. 4 shows another embodiment in which the second CO₂ poor stream 10 is divided into two auxiliary streams 10A and 10B. One of these streams 10A can serve as a purge, while the other 10B is expanded in a turbine 22 and the resulting stream is then recycled upstream of the adsorption unit 3. However, it should be observed that according to an alternative embodiment, the entire stream 10 can be recycled via the turbine 22, which is equivalent to eliminating the line 10A.

[0082] The expanded gas leaving the turbine 22 may optionally be sent to the adsorbers of the adsorption unit 3 during a repressurizing step or during an adsorption step. A recycling method in which the stream 10 is recycled directly to the adsorption unit 3, hence without transiting via a turbine 22, would also be feasible.

[0083] The energy recovered at the shaft of the turbine 22 can either serve to generate electricity, or to drive a compressor.

[0084] It may also be advantageous, as shown in FIG. 5, to heat the gas stream 10B upstream of the turbine 22 via appropriate heating means 16. The gas can thus be heated by direct combustion, by heating in a boiler, or by heat exchange with a fluid available on the site, for example the flue gases issuing from a Cowper stove.

[0085] FIG. 6 shows a first detailed example of a cryogenic unit 9 according to FIGS. 1 to 5 for separating a gas containing CO₂ by partial condensation.

[0086] The first CO₂ rich gas stream 6, that is having a CO₂ content of between 40% and 95%, typically between 60% and 85%, is conveyed by the line 8 (see FIG. 1 to 5) to the cryogenic unit 9. If necessary, the gas can be compressed therein by an additional compressor 55, particularly if it is desirable to slightly raise the pressure of the gas compressed in the intermediate compression unit 7. The compressed gas is then sent to a gas purifying device 33 which, for example, removes the impurities by adsorption through a radial or axial bed in order to prepurify (and/or dry) the CO₂ rich gas, before cooling it below -10° C. This purifier device 33 is periodically regenerated by a gas heated in a regeneration heater (not shown).

[0087] The purified gas recovered by the line 35 is then cooled in a heat exchanger 37 where it is partially condensed. The condensed liquid phase 51 is separated from the gas phase 53 in a phase separator 45.

[0088] The liquid part 51 is sent to a storage unit 49 after expansion in a pressure reducing valve 70, while the gas part 53 is sent to a second heat exchanger 43 where it is partially condensed.

[0089] The partially condensed phase 54 is separated from the gas phase 61 in a phase separator 47. The liquid stream 57

withdrawn from the phase separator 47 is sent to the storage unit 49, after expansion, here also in a pressure reducing valve 71.

[0090] The gas stream 59 issuing from the storage unit 49 is sent successively to the heat exchangers 43 and 37 in order to utilize the refrigerating capacity it contains, before being recycled to the additional compression means 55, if such means are present in the cryogenic unit 9, or, in the absence thereof to an intermediate step of the intermediate compressor 7 located between the adsorption units 3 and the cryogenic unit 9.

[0091] The stream 10 issuing from the phase separator 47 is also sent successively to the heat exchangers 43 and 37 in order to utilize the refrigerating capacity it contains.

[0092] The liquid product 11 containing at least 90% CO₂ is withdrawn from the storage unit 49.

[0093] The refrigerating capacity for liquefaction in the heat exchangers 37 and 43 is supplied by two conventional refrigerating cycles 39, 41, which may optionally be coupled.

[0094] FIG. 7 shows a second example of a cryogenic unit 9 usable in the installations described in FIGS. 1 to 5, which serves to carry out a purification and produce CO₂ at high pressure, that is up to about 60 bar, hence ready to be transported by gas lines.

[0095] As previously, the gas stream 8 having a CO₂ content of between 40% and 95%, typically between 60% and 85%, is compressed (at 55) then purified (at 33) and cooled in the heat exchanger 37 where it is partially condensed. Here also, the condensed phase 51 is separated from the gas phase 53 in a phase separator 45.

[0096] The gas part 53 is sent to a second heat exchanger 43 where it is partially condensed. The partially condensed phase 54 is separated from the gas phase in a phase separator 47. The liquid stream 57 withdrawn from the phase separator 47 is expanded and sent successively to the heat exchangers 43 and 37 in order to utilize the refrigerating capacity it contains.

[0097] The gas stream issuing from the phase separator 47 is sent successively to the heat exchangers 43 and 37 in order to utilize the refrigerating capacity it contains.

[0098] The liquid part 51 issuing from the first phase separator 45 is also expanded and sent successively to the heat exchangers 43 and 37 in order to utilize the refrigerating capacity it contains.

[0099] The streams 67 and 68 are then combined and compressed to a pressure necessary for transport by gas lines. If the combined stream 69 is a two-phase stream, it is heated to make it completely gaseous before being sent to the compressor 73, and then conveyed it via the line 11. This product stream, conveyed via the line 11, is formed of CO₂ having a purity of at least 90%, typically at least 90 to 96%.

1-17. (canceled)

18-34. (canceled)

35. An integrated method using an adsorption unit and a cryogenic unit, in which a feed gas containing CO₂ is sent to the adsorption unit where it is separated into a first CO₂ enriched stream and a first CO₂ depleted stream, the first CO₂ enriched stream being sent to the cryogenic unit where it is separated into a second CO₂ rich stream and a second CO₂ depleted stream, wherein the first CO₂ enriched stream issuing from the adsorption unit contains between about 40% and about 95% CO₂ preferably between about 60% and about 85% CO₂, and is sent to gas homogenizing means for attenuating cyclic variations in pressure, flow rate and/or composi-

tion of said gas, and is then subjected to at least one intermediate compression step before it enters the cryogenic unit.

36. The method of claim 35, wherein the gas homogenizing means comprise at least one storage vessel or reservoir, the vessel or reservoir being preferably maintained at a substantially constant pressure.

37. The method of claim 35, wherein the first CO₂ enriched stream issuing from the adsorption unit has a pressure lower than about 4 bar, and preferably lower than about 2 bar.

38. The method of claim 35, wherein the second CO₂ rich stream issuing from the cryogenic separation unit has a CO₂ content above about 80%, preferably above about 90%, and even more preferably above about 95%.

39. The method of claim 35, wherein at least part of the second CO₂ depleted gas leaving the cryogenic unit is returned to the adsorption unit.

40. The method of claim 39, wherein at least part of the second CO₂ depleted gas leaving the cryogenic unit is returned either to the suction inlet of a compressor feeding the adsorption unit, or upstream of the adsorber(s) of the adsorption unit, or in the adsorber(s) of the adsorption unit during a repressurizing step, in cocurrent or countercurrent, or during an adsorption step.

41. The method of claim 35, wherein a refrigerating unit of the cryogenic unit is also used to cool the feed gas entering the adsorption unit.

42. The method of claim 35, wherein the first CO₂ depleted stream produced by the adsorption unit is expanded in a turbine to produce refrigerating capacity for the cryogenic unit.

43. The method of claim 35, wherein at least part of the second CO₂ depleted gas leaving the cryogenic unit is expanded in a turbine.

44. The method of claim 43, wherein at least part of the second CO₂ depleted gas expanded in a turbine is recycled to the adsorption unit.

45. The method of claim 44, wherein the expanded second CO₂ depleted gas is recycled either to the suction inlet of a

compressor feeding the adsorption unit, or upstream of the adsorber(s) of the adsorption unit, or in the adsorber(s) during a repressurizing step, in cocurrent or countercurrent, or during an adsorption step.

46. The method of claim 43, wherein before entering the turbine, the recycled gas is previously heated.

47. The method of claim 35, wherein at least part of the CO₂ enriched stream compressed in the intermediate compression step is cooled to a temperature above about 0° C., and the liquid part which condenses is preferably removed.

48. The method of claim 35, wherein the incondensable compounds leaving the cryogenic unit are sufficiently cooled to freeze CO₂ in the form of dry ice and to separate the CO₂ thereby frozen from the stream containing the incondensable compounds.

49. An integrated installation for producing CO₂ from a feed gas containing CO₂ comprising:

- a) an adsorption unit for separating the gas containing CO₂ into a first CO₂ enriched stream and a first CO₂ depleted stream the adsorption unit feeding a cryogenic unit with said first CO₂ enriched stream, and
- b) a cryogenic unit for separating the first CO₂ rich stream issuing from the adsorption unit and producing a second CO₂ rich stream and a second CO₂ poor stream,

wherein it further comprises gas homogenizing means for attenuating cyclic variations in pressure, flow rate and/or composition of said gas, and intermediate compression means, arranged on the path of the first CO₂ enriched stream, between the adsorption unit and the cryogenic unit.

50. The installation of claim 32, wherein the gas homogenizing means comprise at least one storage vessel or reservoir.

51. The installation of claim 32, wherein the intermediate compression means comprise one or a plurality of gas compressors.

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