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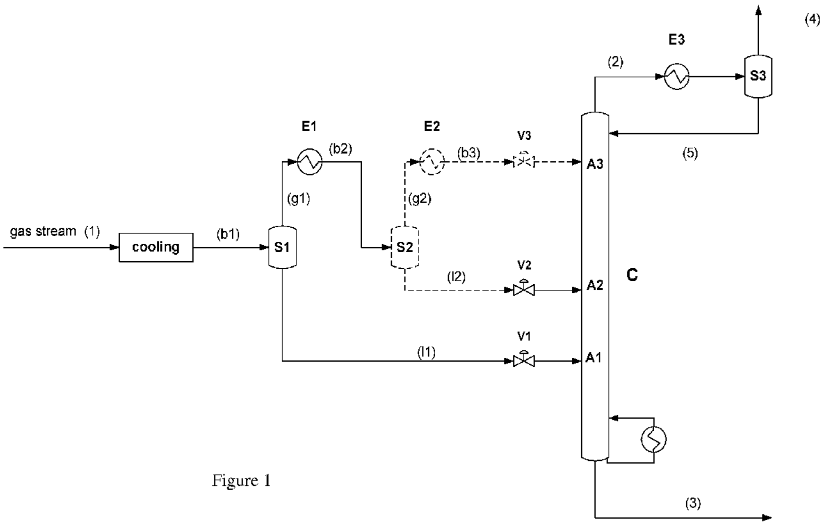

Figure 1

(57) Abstract: The present invention concerns a method for treating a pre-dehydrated feed gas stream containing carbon dioxide and methane, such as pre-dehydrated natural gas stream, by cryogenic separation to obtain a gaseous stream enriched in methane and a liquid stream enriched in carbon dioxide. The invention also concerns a device for carrying out said method.

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CRYOGENIC SEPARATION PROCESS OF A FEED GAS STREAM CONTAINING CARBON DIOXIDE AND METHANE

Field of the invention

The present invention concerns a method for treating a pre-dehydrated feed gas stream containing carbon dioxide and methane, such as pre-dehydrated natural gas stream, by cryogenic separation to obtain a gaseous stream enriched in methane and a liquid stream enriched in carbon dioxide. The invention also concerns a device for carrying out said method.

Technical background

Natural gas or gases associated to oil productions, produced from geological reservoirs often contains acid contaminants, such as carbon dioxide or hydrogen sulphide. In particular, dioxide carbon can be present in large amounts up to 70% molar or over. For most of the applications of these gas streams, the contaminants need to be removed, either partially or almost completely, depending on the application and the contaminant.

Methods to lower the carbon dioxide content of a hydrocarbon stream are known in the art.

The most common process involves the use of amine solvents. This method is very selective towards hydrocarbons and allows obtaining a gas having less than 50 ppm of carbon dioxide, as required for LNG plants. However, this method requires a high amount of energy for the regeneration of the solvent, as well as for the reinjection of carbon dioxide in the reservoir. Therefore, it is not suitable for treating a gas stream containing high contents of carbon dioxide.

Another method involves the use of semi-permeable membranes. This method is known as a bulk treatment, advantageous for gas streams containing large contents of carbon dioxide. However, when several membranes are used in series to concentrate the carbon dioxide in the permeate, it requires intermediate compression steps. Furthermore, if carbon dioxide is to be re-injected into the reservoir, it also requires a final compression step, which increases the energetic cost of the process. Energy comparisons show that the membranes become less attractive than cryogenic separation discussed hereafter, in the range of 40-50% CO2 raw gas where the cryogenic distillation process becomes more advantageous.

Another method is the cryogenic separation, which generally involves a distillation column. This method is energetically advantageous for gas streams containing high contents of carbon dioxide. In order to optimize the thermal energy, the process typically comprises a system which enables recovery of thermal energy from several cold streams, such as from the treated gas or from the liquid carbon dioxide obtained at the bottom the column. The feed gas stream is pre-cooled by heat exchange with said cold streams before it enters in the distillation column.

Though this method is energetically attractive, the drawback of such pre-cooling steps is an increased risk of crystallisation of paraffinic hydrocarbons and the formation of hydrates in the heat exchangers or the downstream conduits during the pre-cooling stage, especially in the heat exchanger working at the lowest temperature.

Said drawback can be avoided by pre-treating the feed gas stream in order to remove the heaviest hydrocarbons from the feed gas stream before it goes through the heat exchangers which perform the pre-cooling stage. Typically, this can be done with an upstream fractionation column equipped with a rectifying section. However, this solution involves an heavy equipment and is expensive to perform.

For instance, WO 99/01707 describes a rectification column upstream the main CO2 separation column as a way to remove the wax contained in the feed gas. Said rectification is a classical way to remove wax components from a natural gas to eliminate the risk of plugging the downstream equipments by wax, and specifically the heat-exchangers.

Alternatively, the crystallisation of paraffinic hydrocarbons may be prevented by limiting the pre-cooling temperature and by letting the complementary cooling being made in the distillation column. In this way, the heaviest fractions of the gas are eliminated, tray by tray, in the rectification section below the coolest zone of the distillation. However, this method is more energy-consuming, as the cold is brought in the coldest part of the process, i.e. the reflux system.

Therefore, there is need for a cryogenic distillation method that removes acid components, such as carbon dioxide, from a hydrocarbon stream containing carbon dioxide and methane, such as a natural gas stream, with reduced energy consumption and reduced installation costs that allows to prevent the risks of crystallisation of paraffinic hydrocarbons in the pre-cooling stage, and more specifically in the heat exchangers.

Summary of the invention

An object of the present invention is a method for treating a pre-dehydrated feed gas stream containing carbon dioxide and methane (1) to obtain a gas stream enriched in methane (4) and a liquid stream enriched in carbon dioxide (3), said method comprising:

(1) providing the pre-dehydrated feed gas stream containing carbon dioxide and methane (1);

(2) cooling the gas stream containing carbon dioxide and methane (1) thereby forming a biphasic stream (b1);

(3) introducing said biphasic stream (b1) in a gas/liquid separator S1, thereby separating a liquid fraction (l1) and a gaseous fraction (g1);

(4) expanding the liquid fraction (l1) and feeding it into a distillation column C at a feeding point A1;

(5) cooling the gaseous fraction (g1) by means of a heat exchanger E1 thereby forming a biphasic stream (b2);

(6) expanding the biphasic stream (b2) and feeding it into the distillation column C at a feeding point A2 which is higher than feeding point A1;

(7) subjecting the streams fed into the distillation column C to distillation thereby recovering the a gas stream enriched in methane (2) at the top of the column

and the liquid stream enriched in carbon dioxide (3) at the bottom of the column;

(8) partially condensing and introducing the gas stream enriched in methane (2) into a gas / liquid separator S3 thereby recovering the gaseous fraction enriched in methane (4) and a liquid fraction enriched in carbon dioxide (5),

(9) feeding the liquid fraction enriched in carbon dioxide (5) into the top of the column as a reflux.

According to the present invention, the feed gas stream is pre-cooled before entering into the distillation column by passing it through heat exchanger(s). Pre-cooling of the gas stream can also be performed by using expansion device(s) in addition to heat exchanger(s).

As mentioned previously, a drawback of a deep pre-cooling is an increased risk of crystallisation of paraffinic hydrocarbons or formation of hydrates in the heat exchangers or the downstream conduits, and more especially in the heat exchanger working at the lowest temperature, which may ultimately lead to plugging. This risk can be eliminated if the feed gas stream is preliminary subjected to a severe pre-treatment to remove enough water and heavy hydrocarbon components (containing paraffinic hydrocarbons) from the feed stream upstream of the pre-cooling stage.

An object of the present invention is to provide a method for treating a hydrocarbon gas stream containing acid contaminants, such as carbon dioxide, that allows reducing the amounts of water and of heavy hydrocarbon components from the gaseous stream during the pre-cooling treatment, and thus to eliminate the need of severe upstream pre-treatments.

It has been found that the risks of crystallisation of paraffinic hydrocarbons and hydrates on the surface of said heat exchanger(s) or the downstream conduits can be reduced if at least one liquid/gas separator is placed upstream of said heat exchanger(s). Preferably, one liquid/gas separator is positioned upstream each heat exchanger.

After separation, the liquid fraction is depleted with methane and tends to be enriched with the crystallisation-generating components (e.g. the heaviest paraffinic hydrocarbons and water). The liquid/gas separator makes possible that only the gaseous fraction depleted with the crystallisation-generating components passes through the heat exchanger(s), whereas the liquid fraction enriched with the crystallisation-generating components is directly fed into the distillation column in a temperature zone where crystallisation cannot occur. Therefore, the risk of plugging the heat exchanger(s) or the downstream conduits with paraffinic waxes and hydrates is suppressed.

In practice, the method of the invention has the following advantages:

- the risk of plugging the heat exchanger(s) with waxes and hydrates is significantly reduced;
- with a limited dehydration around 50 ppm water, and a typical pre-cooling to -30°C, the method of the invention allows to achieve a water margin versus hydrate formation above 50% (reference to the tables 2 and 3) ;
- the pre-dehydration treatment of the feed gas stream can be made to a lower specification, possibly with a more accessible technology, than the same method having no gas/liquid separator before the heat exchanger(s);
- the pre-treament to remove the heavy components from the gas and the associated risks of wax deposit in the heat exchanger(s), can be avoided, compared to the same method having no gas/ liquid separator before the heat exchanger(s);
- either a refrigeration loop or the treated gas or liquid carbon dioxide recovered at the bottom of the distillation column, or preferably a combination of them, can be used to pre-cool the feed gas stream;
- the liquid carbon dioxide recovered at the bottom of the distillation column can be re-injected in geological reservoir, after pressurisation by pumps and not compressors;
- the method can be combined with a finishing sweetening treatment, such as a permeation membrane unit or an amine unit, to obtain a treated gas with even lower concentration of carbon dioxide and ;

- less energy is consumed compared to the same method having no gas/liquid separator before the heat exchanger(s) since the feed gas stream is partially condensed and the liquid fractions l_1 and l_2 separated from the gas streams are fed into the distillation column, without passing through the heat exchangers.

According to the method of the invention, a variety of heat exchangers, gas/liquid separators and expansion devices can be suitably used.

Heat exchangers include shell and tubes heat exchangers, as well as multipass exchangers which are especially adapted to recover thermal energy of different sources such as those using Plate Fin Heat Exchangers (PFHE) or Printed Circuit heat Exchangers (PCHE). Preferred heat exchangers are those adapted to multi-passes PFHE or PCHE exchanges. They allow a more efficient and complete heat recovery than heat exchangers in series while remaining compact.

Gas/liquid separators include cyclonic separators and gravity separators. Preferred gas/liquid separators are gravity separators completed with specific internals to improve the separation of small droplets, such as wiremesh or vane packs.

Expansion devices include common expanders, turbo expanders, laval nozzles, valves, flash valves, in particular Joule-Thomson expansion valves. Expanders can only be used for a monophasic stream while valves can be used for biphasic or monophasic streams. Preferred valves are Joule –Thomson expansion valves.

Step (1)

The feed gas stream (1) treated by the method of the present invention may be any suitable gas stream containing carbon dioxide and methane, but is usually a natural gas stream obtained from natural gas or petroleum reservoirs.

In step (1), a pre-dehydrated feed gas stream is provided. It means that the feed gas stream was preliminary subjected to a dehydration (or drying) treatment in order to partially or completely remove water from the feed gas stream. This can be done for instance with drying agents such as glycol, MEG (monoethylene glycol), DEG (diethylene glycol), TEG (triethylene glycol), glycerol, silica gel or alumina oxide or with molecular sieves, e.g. zeolites. Those methods are well known to persons skilled in the art.

The amount of water in the pre-hydrated feed gas stream (1) is preferably less than 100 ppm mole, more preferably less than 50 ppm mole, even more preferably less than 30 ppm mole.

In addition, the method according to the present invention can comprise before step (2), a step for removing at least partially the hydrocarbon components heavier than methane from the feed gas stream (1). This can be done for instance by using separator(s), filter-coalescer(s), fractionation column(s), or membrane(s). The removed hydrocarbon components heavier than methane are optionally recovered.

Depending the amount of hydrocarbon components heavier than methane, simple devices, such as separators or filter-coalescers after some cooling will be used by preference. More sophisticated devices, such as a fractionation column, may be used if mandatory for the downstream process. However, they may be uneconomical just for additional HC recovery purpose, and in most of the cases, it may be preferable to let these hydrocarbons within the feed stream (1) and finally in the carbon dioxide (3) which is produced at the bottom of the distillation column. The feed gas stream may be also pre-treated to remove other contaminants such as H_2S, other sulphur compounds, mercury, etc... As these steps are well known to the person skilled in the art, they are not further discussed here.

The amount of hydrocarbon components heavier than methane in the pre-hydrated feed gas stream (1) is preferably less than 5 mol %, more preferably less than 3 mol %, even more preferably less than 2 mol %.

Typically, the pre-dehydrated feed gas stream (1) comprises from 10 to 60 molar % of methane and 40 to 90 molar % of carbon dioxide, preferably from 20 to 40 molar % of methane and 60 to 80 molar % of carbon dioxide.

The pre-dehydrated feed gas stream (1) in step (1) can have a temperature between 10 and 50 °C, preferably between 20 and 40 °C, more preferably between 25 and 35 °C, and a pressure between 50 and 100 bars, preferably between 60 and 80 bars, more preferably between 65 and 75 bars. The pressure of the pre-dehydrated can be controlled by means of a valve for instance located upstream of the pre-treatment units.

Step (2)

The cooling in step (2) of the pre-dehydrated feed gas stream (1) may be done by methods known in the art. For instance, cooling may be done against an external cooling fluid, such as a refrigerant fluid, by means of heat exchanger(s), or against a cooling fluid which is recycled from the liquid or gas streams exiting the distillation column. If pressure of the feed gas stream is sufficiently high, cooling may be obtained by expansion of the feed gas stream. Combinations of these various ways of cooling are also possible.

The pre-dehydrated feed gas stream (1) is preferably cooled by a combination of heat exchanger(s) and expansion devices.

For instance, the pre-dehydrated feed gas stream (1) can be cooled through a heat exchanger followed by an expansion device such as Joule-Thomson valve. Preferably, this heat exchanger is exchanging with the cold streams of the column, i.e. could be used as a reboiler for the column and / or a liquid pumparound.

Suitably, the feed gas stream is cooled in step (2) to a temperature comprised between -10 °C and +10 °C, preferably between -8 °C and +8 °C, more preferably between -5 °C and +5 °C. In step (2), the pressure of the feed gas stream is comprised between 50 bars and 90 bars, preferably between 60 bars and 80 bars, more preferably 65 bars and 75 bars.

The cooling of the pre-dehydrated feed gas stream containing carbon dioxide and methane (1) in step (2) leads to the formation of a biphasic stream (b_1). The term “biphasic” means that the stream is composed of a mixture of a gaseous phase and a liquid phase.

Step (3)

In step (3), the biphasic stream (b_1) is introduced in a gas/liquid separator S1, thereby separating a liquid fraction (l_1) and a gaseous fraction (g_1).

Preferably, S1 is a gravity separator completed with specific internal to enhance liquid separation efficiency, as wire-mesh pads or vane-packs.

The gaseous fraction (g_1) is enriched with methane. The liquid fraction (l_1) is enriched with carbon dioxide, water and C2+ crystallization-generating components, such as paraffinic components.

Step (4)

In step (4), the liquid fraction (l_1) is expanded with an expansion device V1 and fed into the distillation column C at a feeding point A1.

Expansion of the liquid fraction (l_1) is performed so as to reach the operating pressure of the distillation column, typically between 30 bar and 45 bar, preferably between 32 bar and 42 bar, more preferably between 35 bar and 40 bar.

Expansion device V1 is preferably a Joule-Thomson expansion valve.

Before expansion, the temperature and pressure of the liquid fraction (l_1) are respectively comprised between -10 °C and +10 °C and 50 bar and 90 bar, preferably between -8 °C and +8 °C and 60 bar and 80 bar, more preferably between -5 °C and +5°C and 65 bar and 75 bar.

First embodiment: steps (5) and (6)

In a first embodiment, the gaseous fraction (g_1) in step (5) is cooled by means of a heat exchanger E1 thereby forming a biphasic stream (b_2).

Suitably, the gaseous fraction (g_1) is cooled in step (5) to a temperature comprised between -40 °C and -5 °C, preferably between -35 °C and -10 °C, more preferably between -30 °C and -15 °C. In step (5), the pressure of the gaseous fraction (g_1) is comprised between 50 bar and 90 bar, preferably between 60 bar and 80 bar, more preferably 65 bar and 75 bar.

Heat exchanger E1 is preferably a multi-pass heat exchanger exchanging with several cold sources.

In step (6), the biphasic stream (b_2) is expanded by means of an expansion device V2 to reach the operating pressure of the distillation column as mentioned previously and fed into the distillation column C at a feeding point A2 which is higher than feeding point A1.

V2 is preferably a Joule-Thomson expansion valve.

Before expansion, the temperature and pressure of the biphasic stream (b_2) are respectively comprised between -40 °C and -5 °C and 50 bar and 90 bar, preferably between -35 °C and -10 °C and 60 bar and 80 bar, more preferably between -30 °C and -15 °C and 65 bar and 75 bar.

According to the first embodiment, the distillation column C is fed with two different streams at two different feeding points A2 and A1.

Second embodiment: steps (5a), (5b), (5c), (5d) and (6)

In a second embodiment, a second separator S2 is used downstream of E1 and upstream of the distillation column C. The following steps are performed instead of steps (5) and (6):

(5a) cooling the gaseous fraction (g_1) by means of the heat exchanger E1 thereby forming a biphasic stream (b_2);

(5b) introducing the stream (b_2) in a gas/liquid separator S2, thereby separating a liquid fraction (l_2) and a gaseous fraction (g_2);

(5c) expanding the liquid fraction (l_2) and feeding it into the distillation column C at a feeding point A2 which is higher than feeding point A1;

(5d) cooling the gaseous fraction (g_2) by means of the heat exchanger E2 thereby forming a biphasic stream (b_3);

(6) expanding the biphasic stream (b_3) and feeding it into the distillation column C at a feeding point A3 which is higher than feeding point A2.

A1 and A2 of the second embodiment are not necessarily at the same levels than A1 and A2 of the first embodiment.

Suitably, the gaseous fraction (g_1) is cooled in step (5a) to a temperature comprised between -45 °C and -10 °C, preferably between -40 °C and -15 °C, more preferably between -35 °C and -20 °C. In step (5a), the pressure of the gaseous fraction (g_1) is comprised between 50 bar and 90 bar, preferably between 60 bar and 80 bar, more preferably 65 bar and 75 bar.

Heat exchanger E1 is preferably a multi-pass heat exchanger exchanging with several cold sources.

In step (5b), the stream (b_2) is introduced in a gas/ liquid separator S2, thereby separating a liquid fraction (l_2) and a gaseous fraction (g2).

Gas/liquid separator S2 is preferably a gravity separator completed with specific internals to enhance liquid separation efficiency, such as wire-mesh pads or vane-packs.

The gaseous fraction (g_2) is enriched with methane relatively to the stream (b_2). As a result, the liquid fraction (l_2) is depleted with methane and tends to be enriched with carbon dioxide and other crystallization-generating components, such as paraffinic components and water.

In step (5c), the liquid fraction (l_2) is expanded to reach the operating pressure of the distillation column and fed into the distillation column C at a feeding point A2.

Expansion of the liquid fraction (l_2) is performed by means of an expansion device V2, typically between 30 bar and 45 bar, preferably between 34 bar and 42 bar, more preferably between 36 bar and 40 bar. Expansion device V2 is preferably a Joule-Thomson expansion valve.

Before expansion, the temperature and pressure of the liquid fraction (l_2) are respectively comprised between -10 °C and -45 °C and 50 bar and 90 bar, preferably between -15 °C and -40 °C and 60 bar and 80 bar, more preferably between -20 °C and -35 °C and 65 bar and 75 bar.

In step (5d), the gaseous fraction (g_2) is suitably cooled by means of heat exchanger E2 to a temperature comprised between -50 °C and -20 °C, preferably between -45 °C and -25 °C, more preferably between -40 °C and -30 °C.

Heat exchanger E2 is preferably a multi-pass heat exchanger exchanging with several cold sources.

In step (5d), the pressure of the gaseous fraction (g_2) is comprised between 50 bar and 90 bar, preferably between 60 bar and 80 bar, more preferably 65 bar and 75 bar.

In step (6) of the second embodiment, the biphasic stream (b_3) is expanded and fed into the distillation column C at a feeding point A3 which is higher than feeding point A2.

Before expansion, the temperature and pressure of the biphasic stream (b_3) are respectively comprised between -50 °C and -20 °C and 50 bar and 90 bar, preferably between -45 °C and -25 °C and 60 bar and 80 bar, more preferably between -40 °C and -30 °C and 65 bar and 75 bar.

Expansion of the biphasic stream (b_3) is performed with an expansion device V3 to reach the operating pressure of the distillation column as mentioned previously. Expansion device V3 is preferably a Joule-Thomson expansion valve.

According to the second embodiment, as a result of the two gas/liquid separators S1 and S2, the distillation column C is fed with three different streams at three different feeding points A1, A2 and A3.

The method is not limited to one or two gas/liquid separators. For instance, the method may include more than two heat exchangers upstream of the distillation column. In that case, it may be advantageous to include one gas/liquid separator upstream of each heat exchanger. As a result, if the method uses n separators, the distillation column will be fed with n + 1 different streams.

Step (7)

In step (7), the streams fed into the distillation column C are subjected to distillation thereby recovering the gas stream enriched in methane (2) at the top of the column and the liquid stream enriched in carbon dioxide (3) at the bottom of the column.

By “distillation column”, it is meant a separation structure equivalent to several theoretical trays, equipped with a reboiling system at the bottom that provides hot thermal energy and with a reflux system at the top that provides cold thermal energy.

The reboiler allows to control the temperature at the bottom of the distillation column C and to adjust the methane losses in the liquid stream enriched in carbon dioxide (3).

A variety of distillation columns may be suitably used, such as a column having distillation trays or a column packing (random or structured).

In the distillation column C, part of the carbon dioxide is separated from the methane by distillation. A gas stream enriched in methane (2) is recovered at the top of the column and a liquid stream enriched in carbon dioxide (3) is recovered at the bottom of the column. Hydrocarbons heavier than ethane, and a part of ethane of the feed stream are taken in the liquid stream enriched in carbon dioxide (3). The operating conditions of the distillation column C are chosen so that the crystallisation zone of the carbon dioxide is avoided. Typically, the temperature of the distillation column is controlled by using a reboiler at the bottom of the column and a reflux system at the head of the column.

Typically, the distillation column operates at a pressure comprised between 30 bar and 45 bar, more preferably between 35 bar and 40 bar, and at a minimal treatment temperature, reflux drum included, comprised between - 40 °C and - 70°C, preferably between - 45 °C and -60 °C, more preferably between -53 °C and -56 °C. This operating range corresponds to the gas/liquid equilibrium zones of a mixture comprising carbon dioxide and gaseous hydrocarbons in the coolest area of the process and allows performing separation by distillation without crystallizing carbon dioxide.

Step (8)

The gas stream enriched in methane (2) recovered at the top of the column is partially condensed and introduced into a reflux drum, which is a gas / liquid separator S3, thereby recovering a liquid fraction enriched in carbon dioxide (5) and a gaseous fraction enriched in methane (4).

The gaseous stream (4) has a temperature comprised between -70 °C and -40 °C, preferably between -60 °C and -45 °C, more preferably between -55 °C and -45 °C. The pressure of the gaseous stream (4) can be comprised between 45 bar and 30 bar, preferably between 32 bar and 42 bar, more preferably 35 bar and 40 bar.

The control of the cooling at the top of the column, for instance by means of a refrigeration loop, allows to adjust the CO_2-content specification of the gaseous fraction enriched in methane (4).

Step (9)

The liquid fraction (5) is fed into the top of the distillation column as a reflux by means of a pump followed by an expansion device, preferably a valve.

Pre-cooling

According to the method of the invention, in steps (5) or (5a) and (5d) the feed stream is cooled by means of heat exchanger(s) upstream the distillation (in the pre-cooling system). This may be done by using an external cooling loop, by using cold internal process stream(s) such as the gaseous fraction enriched in methane (4), or by using an open loop using the liquid stream enriched in carbon dioxide (3) as a refrigerant.

In one embodiment, an external refrigerant fluid and possibly the gaseous fraction enriched in methane (4) are used for cooling the feed gas stream, in particular the gaseous fraction (g_1) through heat exchanger E1 and the gaseous fraction (g_2) through heat exchanger E2 if applicable. The same or different external refrigerant fluid may be used for cooling the gas stream enriched in methane (2) through heat exchanger E3 if applicable.

The gaseous fraction enriched in methane (4) may also be used for cooling the gaseous fraction (g_1) through heat exchanger E1, for cooling the gaseous fraction (g_2) through heat exchanger E2 if applicable and/or for cooling the gas stream enriched in methane (2) through heat exchanger E3 if applicable.

Preferably, both an external refrigerant fluid and the gaseous fraction enriched in methane (4) are used for cooling the gaseous fraction (g_1) through heat exchanger E1, for cooling the gaseous fraction (g_2) through heat exchanger E2 if applicable and for cooling the gas stream enriched in methane (2) through heat exchanger E3 if applicable.

For instance, the cooling may be done with an external cooling loop, especially with an external refrigerant loop, e.g. ethylene/propane loop, ethane/propane loop, or CO_2/HFC (hydrofluorocarbons) loop. For safety reasons, the CO_2/HFC refrigerant could be preferable for off-shore installations.

Additionally, the liquid stream enriched in carbon dioxide (3) obtained in step (7) may be pumped and passed through a heat exchanger for cooling the external refrigerant fluid.

In another embodiment, a portion of the liquid stream enriched in carbon dioxide (3) obtained in step (7) can be pumped for providing a recycled liquid stream enriched in carbon dioxide and said recycled liquid stream enriched in carbon dioxide is passed through heat exchanger E1 for cooling the gaseous fraction (g_1), through heat exchanger E2 for cooling gaseous fraction (g_2) if applicable and through heat exchanger E3 for cooling the gas stream enriched in methane (2) if applicable. This particular cooling embodiment is described for instance in WO 2011/135538 which is herein incorporated by reference, and mentioned as an Open Loop.

According to a preferred embodiment, the liquid stream enriched in carbon dioxide (3) obtained in step (7) is not passed through heat exchanger E1 and/or E2 and/or E3 if applicable or is not used as an Open Loop.

<u>Liquid stream enriched in carbon dioxide (3)</u>

According to the present invention, the liquid stream enriched in carbon dioxide (3) obtained in step (7) can be totally or partially injected into a geological reservoir.

As mentioned above, the liquid stream enriched in carbon dioxide (3) can be passed through a heat exchanger for cooling the external refrigerant fluid or can be pumped for providing a recycled liquid stream enriched in carbon dioxide which is used as a refrigerant and passed through heat exchanger E1 for cooling the gaseous fraction (g_1).

Gaseous fraction enriched in methane (4)

Typically, the gaseous fraction enriched in methane (4) comprises from 65 to 85 molar % of methane and from 15 to 35 molar % of carbon dioxide, preferably from 75 to 82 molar % of methane and from 18 to 25 molar % of carbon dioxide.

If desired, the gaseous fraction enriched in methane (4) can be further treated to remove carbon dioxide (finishing treatment). It may be necessary if the feed gas stream has a high content of carbon dioxide.

For instance, the gaseous fraction enriched in methane (4) may be passed through a permeation membrane unit thereby recovering a gaseous stream enriched in methane (6). Preferably, the permeate is recycled upstream of the pre-cooling system, directly into the distillation column C or in the reflux system of the column C.

Other techniques may used to further remove carbon dioxide such as amine treatment, possibly in combination with a permeation membrane unit.

Device

The present invention also relates to a device for carrying out the method as described above, as well as the purified gas stream obtained by the present process.

The device of the present invention comprises:

- a distillation column C fed by at least two distinct feeding points A1 and A2, wherein A2 is higher than A1;
- a cooling means for partially condensing the feed gas stream (1);
- a first gas/liquid separator S1 comprising a liquid phase conduit L1 and a gaseous phase conduit G1, wherein the liquid phase conduit L1 has an expansion device V1and is connected to the feeding point A1;
- a heat exchanger E1 wherein the input of E1 is connected to the gaseous phase conduit G1 and the output of E1 has an expansion device V2 and is connected to the feeding point A2,
- a reflux drum at the top of column C.

In a particular embodiment, the method includes two gas/liquid separators. In that case, the device for carrying out the method comprises:

- a distillation column C fed by at least three distinct feeding points A1, A2 and A3, wherein A2 is higher than A1 and A3 is higher than A2;
- a cooling means for partially condensing the feed gas stream (1);
- a first gas/liquid separator S1 comprising a liquid phase conduit L1 and a gaseous phase conduit G1,
- a second gas/liquid separator S2 comprising a liquid phase conduit L2 and a gaseous phase conduit G2;
- a first heat exchanger E1;
- a second heat exchanger E2;

wherein:

- the liquid phase conduit L1 has an expansion device V1 and is connected to the feeding point A1;
- the input of E1 is connected to the gaseous phase conduit G1 and the output of E1 is connected to the input of S2;
- the liquid phase conduit L2 has an expansion device V2 and is connected to the feeding point A2;
- the gaseous phase conduit G2 is connected to the input of E2;
- the output of E2 has an expansion device V3 and is connected to the feeding point A3
- a reflux drum at the top of column C.

Typically, the device comprises a reboiler at the bottom of the distillation column. Said reboiler is used to control the temperature in the lower part of the column and to adjust the methane losses in the liquid stream enriched in carbon dioxide (3).

The device comprises cooling means to carry out pre-cooling of the feed gas stream and the cryogenic distillation. As described above, this may be done by using an external cooling loop, cold internal process stream(s) such as gaseous fraction(s) enriched in methane (4), or an open loop using the liquid stream enriched in carbon dioxide (3) as a refrigerant.

The device may also comprise pre-treatment means located upstream of the cooling means to carry out a dehydration (or drying) treatment of the feed gas stream (1) in order to partially or completely remove water from it. This can be done for instance with drying agents such as glycol, MEG (monoethylene glycol), DEG (diethylene glycol), TEG (triethylene glycol), glycerol, silica gel or alumina oxide or with molecular sieves, e.g. zeolites.

The pre-treatment means may also include means to remove at least partially the hydrocarbon components heavier than methane from the feed gas stream (1). This can be done for instance by using separator(s), filter-coalescer(s), fractionation column(s), or membrane(s).

The pre-treatment means may also comprise means to remove other contaminants such as H_2S, other sulphur compounds (mercaptans) or mercury from the feed gas stream (1). This can be done for instance by using amines treatment or hybrid solvents as those described in FR2896244.

The device may also comprise finishing treatment means to further remove carbon dioxide from the gaseous fraction(s) enriched in methane (4). These means include membrane separators or amine units.

In one embodiment, a refrigerant loop containing a refrigerant fluid, preferably a mixed refrigerant, such as ethane/propane, ethylene/propane or CO_2/HFC (hydrofluorocarbons), is used as a source (at least partial) for pre-cooling the feed stream and as a source (at least partial) for cooling the gas stream enriched in carbon dioxide (2) recovered at the head of the column by means of heat exchangers. In this embodiment, the refrigeration system is made of a closed loop system, or of 2 cascading closed refrigeration loops. Each loop contains at least a condenser, a receiver, a subcooler, one or several expansion devices, one or several process exchangers that vaporize at least partially the refrigerant. The gaseous refrigerant is recompressed by means of compressor(s) up to the pressure of the condenser, and recirculated in the loop.

In a second embodiment, pre-cooling can be carried out by using at least a portion of the liquid stream enriched in carbon dioxide (3) obtained in step (7) as a refrigerant in an open loop system. The fluid is generally pumped to ease its transfer. It is expanded, possibly to several pressures depending on the temperature needed, and vaporized in heat exchangers while providing cold to the process. The gaseous refrigerant is recompressed by means of compressor(s) up to the pressure of the condenser and cooled down in the condenser to liquid shape or a liquid equivalent in dense phase. The refrigerant is then transferred to the injection system or to the export system (if the injection to geological reservoir(s) is done on a distant location).

The invention will be further illustrated by means of the following figures.

Figures

Figure 1 represents schematically the method according to the present invention with one gas/liquid separator or with two gas/liquid separators (dotted lines).

Figure 2 represents schematically a comparative separation process having no intermediate gas/liquid separator. Computer-derived simulations were performed to simulate process conditions at various stages in the process of Figure 2. The results of this simulation are provided in table 1.

Figure 3 represents schematically a method according to the present invention with one intermediate gas/liquid separator. Computer-derived simulations were performed to simulate process conditions at various stages in the process of figure 3. The results of this simulation are provided in table 2.

Figure 4 represents schematically the method according to the present invention with two intermediate gas/liquid separators. Computer-derived simulations were performed to simulate process conditions at various stages in the process of figure 4. The results of this simulation are provided in table 3.

In Figure 1, a pre-dehydrated feed gas stream (1) containing carbon dioxide and methane is first cooled, thereby forming a biphasic stream (b_1). Then, this biphasic stream (b_1) is introduced in a gas/liquid separator S1, thereby separating a liquid fraction (l_1) and a gaseous fraction (g_1). Then, the liquid fraction (l_1) is expanded by means of an expansion device V1 and fed into a distillation column C at a feeding point A1. The gaseous fraction (g_1) is cooled by means of a heat exchanger E1 thereby forming a biphasic stream (b_2). In heat exchanger E1, the gaseous fraction (g_1) is cooled at a temperature between -40 °C and -5 °C. The biphasic stream (b_2) is either expanded by means of an expansion device V2 and fed into the distillation column C at a feeding point A2 which is higher than feeding point A1 (1st embodiment) or is introduced into a gas/liquid separator S2, thereby separating a liquid fraction (l_2) and a gaseous fraction (g_2) (2nd embodiment in dotted lines). The liquid fraction (l_2) is expanded by means of an expansion device V2 and fed into the distillation column C at a feeding point A2 which is higher than feeding point A1. The gaseous fraction (g_2) is cooled by means of the heat exchanger E2 thereby forming a biphasic stream (b_3). In heat exchanger E2, the gaseous fraction (g_2) is cooled at a temperature between -20 °C and -50 °C. Then, the biphasic stream (b_3) is expanded by means of an expansion device V3 and fed into the distillation column C at a feeding point A3 which is higher than feeding point A2. The three streams fed into the distillation column C are then subjected to a distillation. As a result, a gas stream enriched in methane (2) is recovered at the top of the column and a liquid stream enriched in carbon dioxide (3) is recovered at the bottom of the column. A reboiler at the bottom of the distillation column C is used to control the temperature in the lower part of the column and to adjust the methane losses in the liquid stream enriched in carbon dioxide (3). The gas stream enriched in methane (2) is partially condensed by means of a heat exchanger E3 and is introduced into a gas/liquid separator S3 (reflux drum), thereby forming a liquid fraction enriched in carbon dioxide (5) and a gaseous fraction enriched in methane (4). In heat exchanger E3, the gas stream enriched in methane (2) is cooled at a temperature between -70 °C and -40 °C. The liquid fraction enriched in carbon dioxide (5) is refluxed into the distillation column C.

Examples

Computer-derived simulations were performed to simulate process conditions at various stages in the processes corresponding to Figures 2, 3 and 4. The results of these simulations are respectively provided in table 1, table 2 and table 3.

Tables 1, 2 and 3 provide the molar composition of the feed gas stream and of the streams obtained at various stages in the process, as well as :

- the water content (ppm mole),
- the water saturation for hydrates (ppm mole). Such value corresponds to the minimum water content in the stream for hydrates to appear,
- the margin towards water saturation (%). Such value corresponds to the difference between the water saturation and the water content, divided by the water saturation,
- the C10+ hydrocarbons content (ppm mole),
- the Wax Appearance Temperature (WAT),
- the temperature margin towards WAT (°C). Such value corresponds to the difference between the temperature of the stream and the WAT.

Tables 1, 2 and 3 respectively show the results of the schemes 2 (without intermediate separation), 3 (with one intermediate separation) and 4 (with two intermediate separations), at the various stages of the cooling chain.

Furthermore, tables 1, 2 and 3 show the benefit of intermediate separations with a higher margin towards hydrates when intermediate separation exists.

Tables 1, 2 and 3 also show the benefit for the Wax Apperance Temperature (WAT) in the given examples where 2 separation steps exists.

The stream analysis is reported schematically since calculations of the Wax Appearance Temperature are made with a more complete analysis detailed up to the C30, and taking into account a paraffinic / non paraffinic distribution.

Results of tables 1, 2 and 3:

Tables 1, 2 and 3 provide the pressure and the temperature of each stream and the stream analysis which is calculated by using SRKM (Soave-Redlich-Kwong equation of state modified Panag. Reid).

Tables 1, 2 and 3 provide specific results about hydrates as follows:

- Water content is the stream water concentration calculated by SRKM,
- Water saturation for hydrates is the minimum calculated value of water content to form hydrates. The calculation is made by Peneloux equation, after matching of coefficients based on results of an extensive laboratory measurement campaign.
- The margin between the water content and the water saturation must be higher that the method uncertainty. As it can be seen in the results, the minimum margin increases from 38% (scheme 1) to 51% (scheme 2) and 65% (scheme 3), which clearly shows the advantage of the schemes with 1 or 2 intermediate separation(s) compared with the scheme without any separation.

Furthermore, tables 1, 2 and 3 provide specific results about the risks of wax as follows :

- concentration of the heavy components in the cold streams(C10+),
- Wax Appearance Temperature (WAT) calculated by using the extensive analysis (with paraffinic / non paraffinic components up to C30+ and Coutinho-Daridon VSLE (Vapor Solid Liquid Equilibrium) equation,
- Margin between the temperature of the streams and the WAT: concerning the flowlines, the smallest margins of schemes 1, 2 and 3 are respectively -4°C/10°C/10°C (hence problematic for the scheme 1). Concerning the heat exchangers, which are the most critical equipment versus deposits, the smallest margin of schemes 1, 2 and 3 are respectively 7°C / 24°C / 37°C, which shows clearly the advantage of the schemes with 1 or 2 intermediate separations

compared with the scheme without any separation, with a higher theoretical margin (in this example).

Table 1: scheme without intermediate separation

		NO INTERMEDIATE SEPARATION		
		Streams		
Stream	***Name*** ***Phase***	**200** **Mixed**	**201** **Mixed**	**231** **Mixed**
Temperature	°C	5,434	-30,000	-41,515
Pressure	BAR	72,000	71,300	38,000
Molecular Weight	G/MOL	36,507	36,507	36,507
Total	KG-MOL/HR	33474,871	33474,871	33474,871
Component Mole Fractions				
	N2	0,029147	0,029147	0,029147
	CO2	0,704386	0,704386	0,704386
	H2S	0,000066	0,000066	0,000066
	METHANE	0,251516	0,251516	0,251516
	ETHANE	0,008790	0,008790	0,008790
	PROPANE	0,002738	0,002738	0,002738
	IC4	0,000659	0,000659	0,000659
	NC4	0,000658	0,000658	0,000658
	IC5	0,000280	0,000280	0,000280
	NC5	0,000186	0,000186	0,000186
	C6	0,000274	0,000274	0,000274
	MCP	0,000091	0,000091	0,000091
	BENZENE	0,000180	0,000180	0,000180
	CH	0,000094	0,000094	0,000094
	C7	0,000161	0,000161	0,000161
	MCH	0,000089	0,000089	0,000089
	TOLUENE	0,000183	0,000183	0,000183
	C8	0,000097	0,000097	0,000097
	EBENZENE	0,000005	0,000005	0,000005
	PXYLENE	0,000063	0,000063	0,000063
	OXYLENE	0,000001	0,000001	0,000001
	C9	0,000088	0,000088	0,000088
	C10+	0,000201	0,000201	0,000201
	H2O	0,000050	0,000050	0,000050

Water content (ppm mole)	50,0	50,0	50,0
Water saturation for hydrates (ppm mole)	337,0	131,0	81,0
Margin towards water saturation (%)	85,2	61,8	**38,3**

C10+ (ppm mole)	201,4	201,4	201,4
WAT (°C)	-37,5	-37,5	-37,6
Temp. margin towards WAT (°C)	42,9	**7,5**	**-3,9**

Table 2: scheme with one intermediate separation

		SCHEME WITH ONE INTERMEDIATE SEPARATION					
		Streams					
Stream Name		**300**	**310**	**311**	**312**	**331**	**332**
Phase		**Mixed**	**Liquid**	**Vapor**	**Mixed**	**Mixed**	**Mixed**
Temperature	°C	5,434	5,434	5,434	-30,000	-13,442	-42,077
Pressure	BAR	72,000	72,000	72,000	71,300	38,000	38,000
Molecular Weight	G/MOL	36,507	40,522	35,718	35,718	40,522	35,718
Total	KG-MOL/HR	33474,871	5501,855	27973,018	27973,018	5501,855	27973,018
Component Mole Fractions							
N2		0,029147	0,009825	0,032947	0,032947	0,009825	0,032947
CO2		0,704386	0,833861	0,678920	0,678920	0,833861	0,678920
H2S		0,000066	0,000088	0,000062	0,000062	0,000088	0,000062
METHANE		0,251516	0,132708	0,274883	0,274883	0,132708	0,274883
ETHANE		0,008790	0,008535	0,008840	0,008840	0,008535	0,008840
PROPANE		0,002738	0,004102	0,002470	0,002470	0,004102	0,002470
IC4		0,000659	0,001269	0,000540	0,000540	0,001269	0,000540
NC4		0,000658	0,001351	0,000522	0,000522	0,001351	0,000522
IC5		0,000280	0,000742	0,000189	0,000189	0,000742	0,000189
NC5		0,000186	0,000530	0,000119	0,000119	0,000530	0,000119
C6		0,000274	0,001024	0,000126	0,000126	0,001024	0,000126
MCP		0,000091	0,000352	0,000040	0,000040	0,000352	0,000040
BENZENE		0,000180	0,000772	0,000063	0,000063	0,000772	0,000063
CH		0,000094	0,000382	0,000037	0,000037	0,000382	0,000037
C7		0,000161	0,000709	0,000054	0,000054	0,000709	0,000054
MCH		0,000089	0,000396	0,000029	0,000029	0,000396	0,000029
TOLUENE		0,000183	0,000864	0,000049	0,000049	0,000864	0,000049
C8		0,000097	0,000458	0,000026	0,000026	0,000458	0,000026
EBENZENE		0,000005	0,000026	0,000001	0,000001	0,000026	0,000001
PXYLENE		0,000063	0,000320	0,000013	0,000013	0,000320	0,000013
OXYLENE		0,000001	0,000003	0,000000	0,000000	0,000003	0,000000
C9		0,000088	0,000448	0,000017	0,000017	0,000448	0,000017
C10+		0,000201	0,001130	0,000019	0,000019	0,001130	0,000019
H2O		0,000050	0,000117	0,000037	0,000037	0,000117	0,000037

Water content (ppm mole)	50,0	116,9	36,8	36,8	116,9	36,8
Water saturation for hydrates (ppm mole)	337,0	788,1	248,3	120,0	330,0	75,0
Margin towards water saturation (%)	85,2	85,2	85,2	69,3	64,6	**50,9**

C10+ (ppm mole)	201,4	1129,9	18,7	18,7	1129,9	18,7
WAT (°C)	-37,5	-26,1	-55,3	-54,6	-23,5	-55,3
Temp. margin towards WAT (°C)	42,9	31,5	60,7	**24,6**	**10,1**	13,2

Table 3: scheme with 2 intermediate separations

		SCHEME WITH 2 INTERMEDIATE SEPARATIONS									
		Streams									
Stream ***Name***		**400**	**410**	**411**	**412**	**420**	**421**	**422**	**431**	**432**	**433**
Phase		**Mixed**	**Liquid**	**Vapor**	**Mixed**	**Liquid**	**Vapor**	**Mixed**	**Mixed**	**Mixed**	**Mixed**
Temperature	°C	5,434	5,434	5,434	-18,000	-18,000	-18,000	-30,000	-13,442	-31,367	-44,643
Pressure	BAR	72,000	72,000	72,000	71,300	71,300	71,300	70,600	38,000	38,000	38,000
Molecular Weight	G/MOL	36,507	40,522	35,718	35,718	37,603	29,358	29,358	40,522	37,603	29,358
Total	KG-MOL/HR	33474,871	5501,855	27973,018	27973,018	21576,115	6396,903	6396,903	5501,855	21576,115	6396,903
Component Mole Fractions											
N2		0,029147	0,009825	0,032947	0,032947	0,019516	0,078250	0,078250	0,009825	0,019516	0,078250
CO2		0,704386	0,833861	0,678920	0,678920	0,750728	0,436718	0,436718	0,833861	0,750728	0,436718
H2S		0,000066	0,000088	0,000062	0,000062	0,000070	0,000035	0,000035	0,000088	0,000070	0,000035
METHANE		0,251516	0,132708	0,274883	0,274883	0,215433	0,475406	0,475406	0,132708	0,215433	0,475406
ETHANE		0,008790	0,008535	0,008840	0,008840	0,009098	0,007973	0,007973	0,008535	0,009098	0,007973
PROPANE		0,002738	0,004102	0,002470	0,002470	0,002842	0,001215	0,001215	0,004102	0,002842	0,001215
IC4		0,000659	0,001269	0,000540	0,000540	0,000647	0,000177	0,000177	0,001269	0,000647	0,000177
NC4		0,000658	0,001351	0,000522	0,000522	0,000632	0,000152	0,000152	0,001351	0,000632	0,000152
IC5		0,000280	0,000742	0,000189	0,000189	0,000236	0,000033	0,000033	0,000742	0,000236	0,000033
NC5		0,000186	0,000530	0,000119	0,000119	0,000149	0,000017	0,000017	0,000530	0,000149	0,000017
C6		0,000274	0,001024	0,000126	0,000126	0,000161	0,000008	0,000008	0,001024	0,000161	0,000008
MCP		0,000091	0,000352	0,000040	0,000040	0,000051	0,000002	0,000002	0,000352	0,000051	0,000002
BENZENE		0,000180	0,000772	0,000063	0,000063	0,000082	0,000002	0,000002	0,000772	0,000082	0,000002
CH		0,000094	0,000382	0,000037	0,000037	0,000048	0,000002	0,000002	0,000382	0,000048	0,000002
C7		0,000161	0,000709	0,000054	0,000054	0,000069	0,000002	0,000002	0,000709	0,000069	0,000002
MCH		0,000089	0,000396	0,000029	0,000029	0,000037	0,000001	0,000001	0,000396	0,000037	0,000001
TOLUENE		0,000183	0,000864	0,000049	0,000049	0,000063	0,000001	0,000001	0,000864	0,000063	0,000001
C8		0,000097	0,000458	0,000026	0,000026	0,000034	0,000001	0,000001	0,000458	0,000034	0,000001
EBENZENE		0,000005	0,000026	0,000001	0,000001	0,000001	0,000000	0,000000	0,000026	0,000001	0,000000

		SCHEME WITH 2 INTERMEDIATE SEPARATIONS									
		Streams									
Stream Name		**400**	**410**	**411**	**412**	**420**	**421**	**422**	**431**	**432**	**433**
Phase		**Mixed**	**Liquid**	**Vapor**	**Mixed**	**Liquid**	**Vapor**	**Mixed**	**Mixed**	**Mixed**	**Mixed**
Temperature	°C	5,434	5,434	5,434	-18,000	-18,000	-18,000	-30,000	-13,442	-31,367	-44,643
Pressure	BAR	72,000	72,000	72,000	71,300	71,300	71,300	70,600	38,000	38,000	38,000
Molecular Weight	G/MOL	36,507	40,522	35,718	35,718	37,603	29,358	29,358	40,522	37,603	29,358
Total	KG-MOL/HR	33474,871	5501,855	27973,018	27973,018	21576,115	6396,903	6396,903	5501,855	21576,115	6396,903
Component Mole Fractions (continued)											
PXYLENE		0,000063	0,000320	0,000013	0,000013	0,000017	0,000000	0,000000	0,000320	0,000017	0,000000
OXYLENE		0,000001	0,000003	0,000000	0,000000	0,000000	0,000000	0,000000	0,000003	0,000000	0,000000
C9		0,000088	0,000448	0,000017	0,000017	0,000022	0,000000	0,000000	0,000448	0,000022	0,000000
C10+		0,000201	0,001130	0,000019	0,000019	0,000024	0,000000	0,000000	0,001130	0,000024	0,000000
H2O		0,000050	0,000117	0,000037	0,000037	0,000046	0,000007	0,000007	0,000117	0,000046	0,000007
Water content (ppm mole)		50,0	116,9	36,8	36,8	45,6	7,3	7,3	116,9	45,6	7,3
Water saturation for hydrates (ppm mole)		337,0	788,1	248,3	172,0	212,9	34,1	37,0	330,0	143,0	27,0
Margin towards water saturation (%)		85,2	85,2	85,2	78,6	78,6	78,6	80,3	**64,6**	68,1	72,9

C10+ (ppm mole)	201,4	1129,9	18,7	18,7	24,2	0,1	0,1	1129,9	24,2	0,1
WAT (°C)	-37,5	-26,1	-55,3	-55,3	-51,2	-87,7	-87,6	-23,5	-51,1	-86,9
Temp. margin towards WAT (°C)	42,9	31,5	60,7	**37,3**	33,2	69,7	57,6	**10,1**	19,7	42,3

CLAIMS

1. A method for treating a pre-dehydrated feed gas stream containing carbon dioxide and methane (1) to obtain a gas stream enriched in methane (4) and a liquid stream enriched in carbon dioxide (3), said method comprising:
   - (1) providing the pre-dehydrated feed gas stream containing carbon dioxide and methane (1);
   - (2) cooling the pre-dehydrated feed gas stream containing carbon dioxide and methane (1) thereby forming a biphasic stream (b_1);
   - (3) introducing said biphasic stream (b_1) in a gas/liquid separator S1, thereby separating a liquid fraction (l_1) and a gaseous fraction (g_1);
   - (4) expanding the liquid fraction (l_1) and feeding it into a distillation column C at a feeding point A1;
   - (5) cooling the gaseous fraction (g_1) by means of a heat exchanger E1 thereby forming a biphasic stream (b_2);
   - (6) expanding the biphasic stream (b_2) and feeding it into the distillation column C at a feeding point A2 which is higher than feeding point A1;
   - (7) subjecting the streams fed into the distillation column C to distillation thereby recovering a gas stream enriched in methane (2) at the top of the column and the liquid stream enriched in carbon dioxide (3) at the bottom of the column.
   - (8) partially condensing and introducing the gas stream enriched in methane (2) into a gas/liquid separator S3 thereby recovering the gaseous fraction enriched in methane (4) and a liquid fraction enriched in carbon dioxide (5),
   - (9) feeding the liquid fraction enriched in carbon dioxide (5)into the top of the column as a reflux.

2. The method according to claim 1, characterized in that a second separator S2 is used downstream of E1 and upstream of the distillation column C and the following steps are performed instead of steps (5) and (6):

(5a) cooling the gaseous fraction (g_1) by means of the heat exchanger E1 thereby forming a biphasic stream (b_2);

(5b) introducing the stream (b_2) in a gas/ liquid separator S2, thereby separating a liquid fraction (l_2) and a gaseous fraction (g_2);

(5c) expanding the liquid fraction (l_2) and feeding it into the distillation column C at a feeding point A2 which is higher than feeding point A1;

(5d) cooling the gaseous fraction (g_2) by means of the heat exchanger E2 thereby forming a biphasic stream (b_3);

(6) expanding the biphasic stream (b_3) and feeding it into the distillation column C at a feeding point A3 which is higher than feeding point A2.

3. The method according to claims 1 or 2, characterized in that a step for removing at least partially the hydrocarbon components heavier than methane from the feed gas stream (1) is performed before step (2).

4. The method according to any one of claims 1 to 3, characterized in that cooling in step (2) includes cooling by means of a heat exchanger.

5. The method according to claim 4, characterized in that a portion of a distillation liquid flowing downward through the distillation column is used for cooling the feed gas stream (1) by means of said heat exchanger.

6. The method according to any one of claims 1 to 5, characterized in that the feed gas stream (1) is expanded during step (2).

7. The method according to any one of claims 1 to 6, characterized in that the column overhead gaseous stream (2) is partially condensed by cooling through a heat exchanger E3.

8. The method according to any one of claims 1 to 7, characterized in that an external refrigerant fluid and possibly the gaseous fraction enriched in methane (4) are used for cooling the gaseous fraction (g_1) through heat exchanger E1, for

cooling the gaseous fraction (g_2) through heat exchanger E2 if applicable and for cooling the gas stream enriched in methane (2) through heat exchanger E3 if applicable.

9. The method according to any one of claims 1 to 8, characterized in that the gaseous fraction enriched in methane (4) is used for cooling the gaseous fraction (g_1) through heat exchanger E1, for cooling the gaseous fraction (g_2) through heat exchanger E2 if applicable and for cooling the column overhead gaseous stream (2) through heat exchanger E3 if applicable.

10. The method according to any one of claims 1 to 10, characterized in that the liquid stream enriched in carbon dioxide (3) obtained in step (7) is totally or partially injected into a geological reservoir.

11. The method according to any one of claims 1 to 11, characterized in that the gaseous fraction enriched in methane (4) is passed through a membrane separator thereby recovering a gaseous stream enriched in methane (6), wherein the permeate is recycled upstream of or directly into the distillation column C.

12. The method according to any one of claims 1 to 12, characterized in that the feed gas stream (1) comprises from 10 to 60 molar % of methane and 40 to 90 molar % of carbon dioxide.

13. The method according to any one of claims 1 to 13, characterized in that the gaseous fraction enriched in methane (4) comprises 65 to 85 molar % of methane and 15 to 35 molar % of carbon dioxide.

14. A device for carrying the method according to any one of claims 1 to 14, comprising:
- a distillation column C fed by at least two distinct feeding points A1 and A2, wherein A2 is higher than A1;
- a cooling means for partially condensing the feed gas stream (1);

- a first gas/liquid separator S1 comprising a liquid phase conduit L1 and a gaseous phase conduit G1, wherein the liquid phase conduit L1 has an expansion device V1 and is connected to the feeding point A1;
- a heat exchanger E1 wherein the input of E1 is connected to the gaseous phase conduit G1 and the output of E1 has an expansion device V2 and is connected to the feeding point A2,
- a reflux drum at the top of column C.

15. The device for carrying the process according to any one of claims 2 to 14, comprising:

- a distillation column C fed by at least three distinct feeding points A1, A2 and A3, wherein A2 is higher than A1 and A3 is higher than A2;
- a cooling means for partially condensing the feed gas stream (1);
- a first gas/liquid separator S1 comprising a liquid phase conduit L1 and a gaseous phase conduit G1,
- a second gas/liquid separator S2 comprising a liquid phase conduit L2 and a gaseous phase conduit G2;
- a first heat exchanger E1;
- a second heat exchanger E2;

wherein:

- the liquid phase conduit L1 has an expansion device V1 and is connected to the feeding point A1;
- the input of E1 is connected to the gaseous phase conduit G1 and the output of E1 is connected to the input of S2;
- the liquid phase conduit L2 has an expansion device V2 and is connected to the feeding point A2;
- the gaseous phase conduit G2 is connected to the input of E2;
- the output of E2 has an expansion device V3 and is connected to the feeding point A3
- a reflux drum at the top of column C.

16. The device according to claims 15 or 16, characterized in that it further comprises a reboiler at the bottom of the distillation column.

17. The device according to any one of claims 15 to 17, characterized in that it further comprises a refrigerant loop containing a refrigerant fluid.

18. The device according to claim 18, characterized in that the refrigerant fluid is a blend of ethane/propane, a blend of ethylene/propane or a blend of CO_2/ hydrofluorocarbons.

19. The device according to any one of claims 15 to 18, characterized in that it further comprises pre-treatment means located upstream of the cooling means, such as drying agent(s), molecular sieve(s), separator(s), filter-coalescer(s), fractionation colum(s), or membrane(s).

20. The device according to any one of claims 15 to 19, characterized in that it further comprises finishing treatment means, such as a membrane separator or an amine unit.

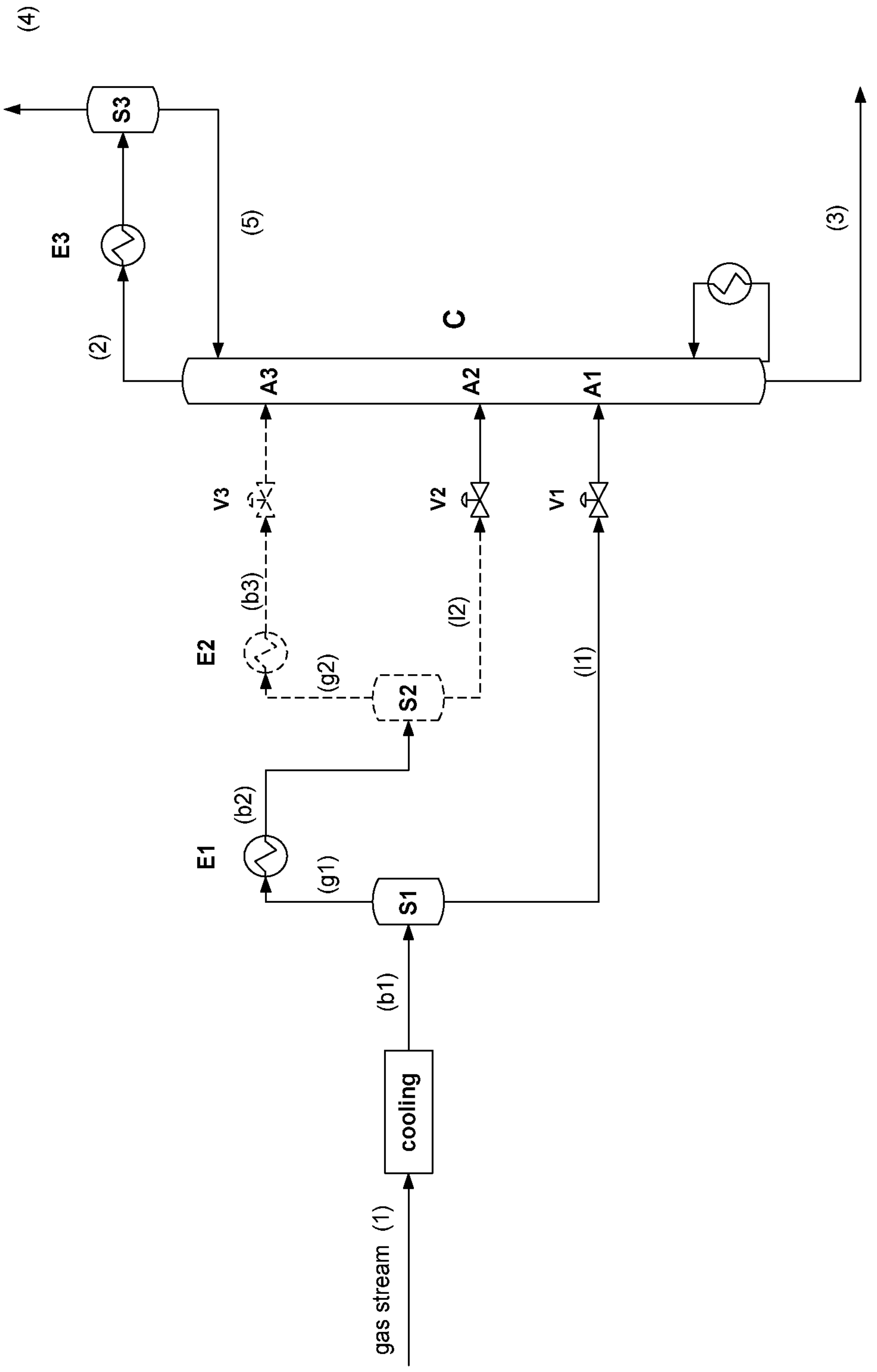
gas stream
(1)
cooling
(b1)
S1
(g1)
E1
(b2)
S2
(g2)
(l2)
E2
(b3)
V3
V2
V1
(l1)
A3
A2
A1
C
(2)
E3
S3
(4)
(5)
(3)

Figure 1

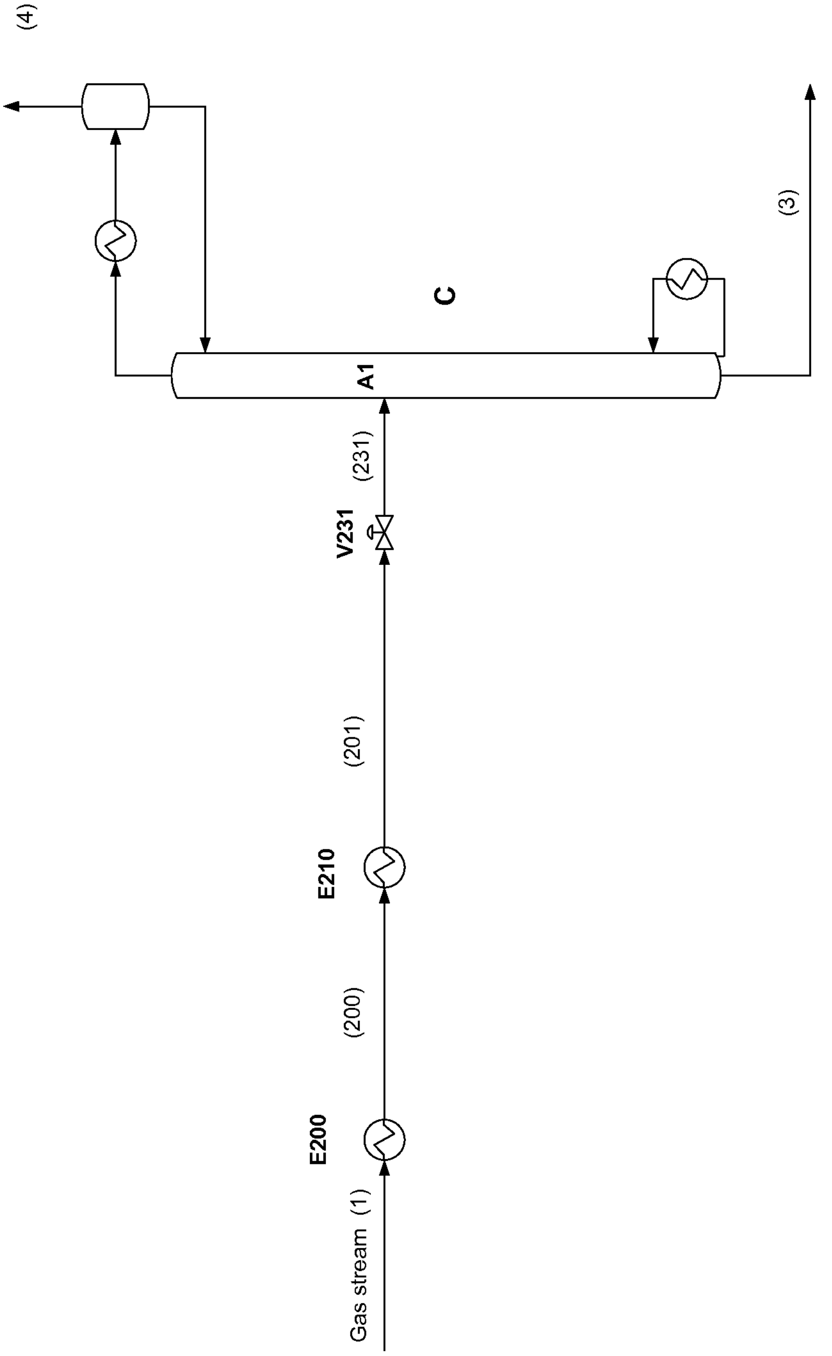

Figure 2

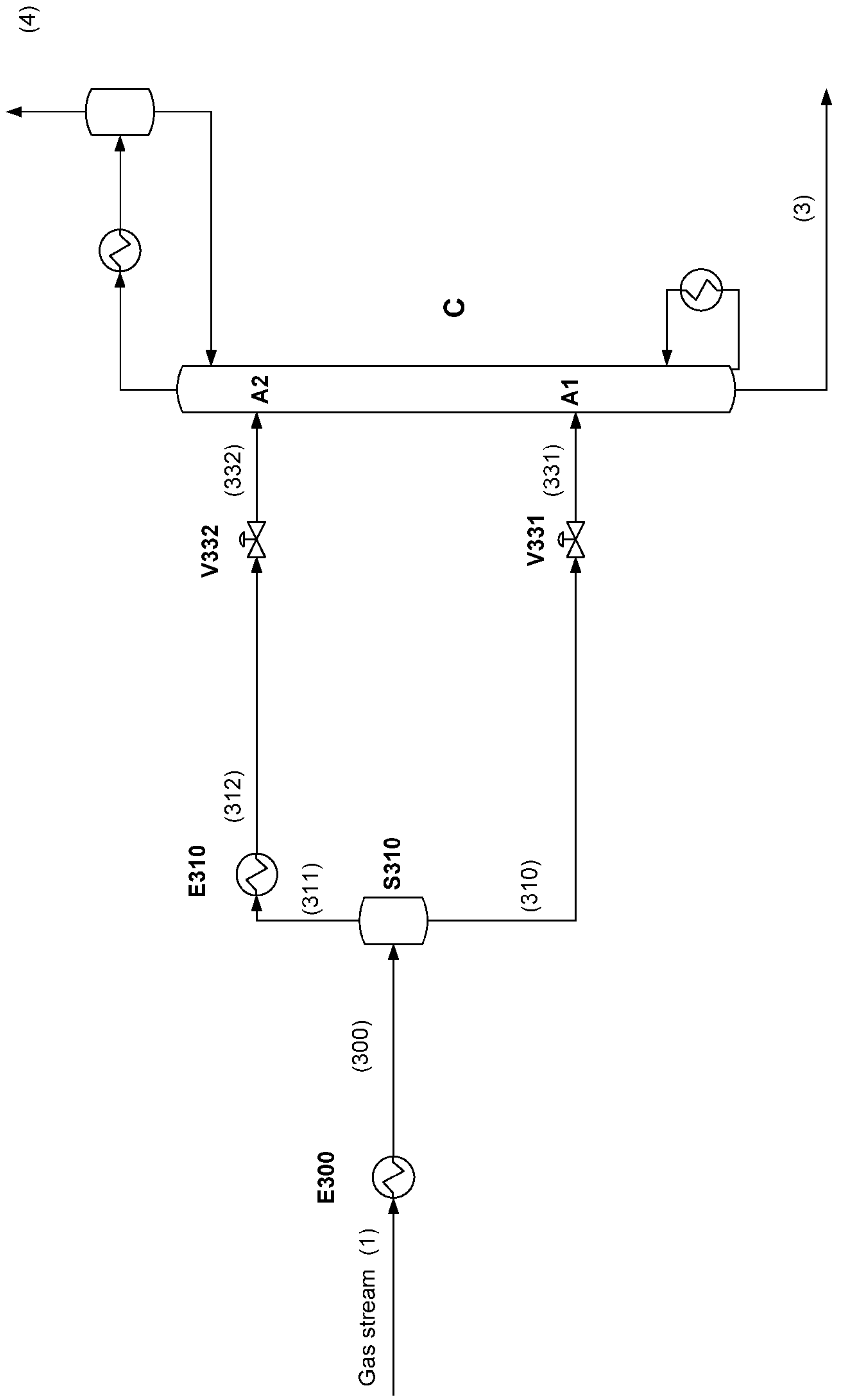
(4)
C
(3)
A2
A1
(332)
(331)
V332
V331
(312)
E310
(311)
S310
(310)
(300)
E300
Gas stream (1)

Figure 3

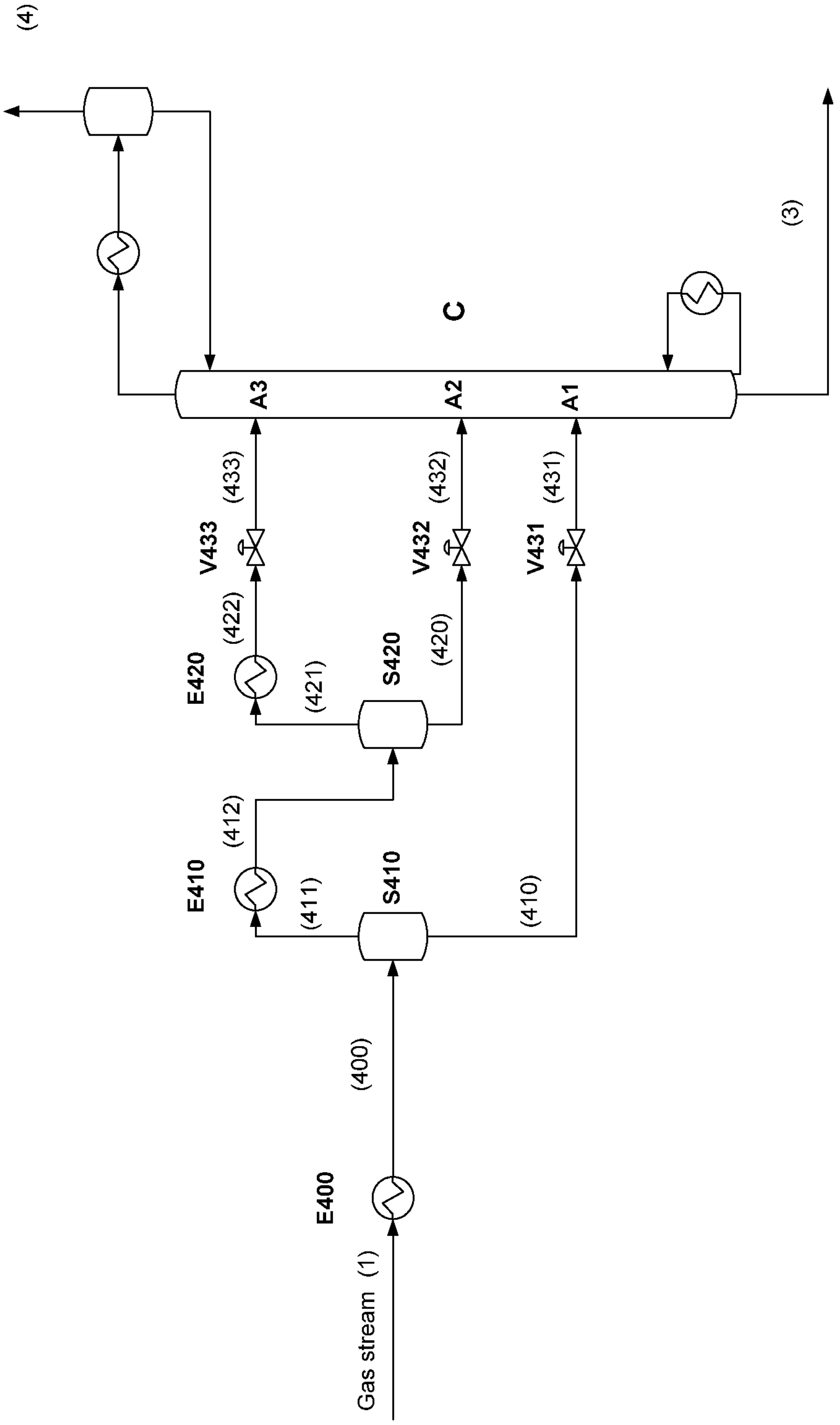
Gas stream (1)
E400
(400)
S410
(410)
(411)
E410
(412)
S420
(420)
(421)
E420
(422)
V431
(431)
V432
(432)
V433
(433)
A1
A2
A3
C
(3)
(4)

Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/000877

A. CLASSIFICATION OF SUBJECT MATTER
INV. F25J3/02 F25J3/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
F25J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2002/065446 A1 (WILKINSON JOHN D [US] ET AL) 30 May 2002 (2002-05-30) paragraphs [0009], [0015], [0018], [0036]; figures 2,5; table 2 -----	1,2,4-7, 9,14-16 1-20
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search 15 October 2012	Date of mailing of the international search report 24/10/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schopfer, Georg

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/000877

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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