

Method and device for the membrane separation of a mixture containing
predominantly hydrogen and carbon dioxide

The present invention relates to a process for membrane separation of a mixture containing predominantly hydrogen and carbon dioxide and additionally at least one other component chosen from carbon monoxide, methane and nitrogen.

A mixture containing predominantly hydrogen and carbon dioxide has a composition such that at least 50 mol% of the mixture is composed of hydrogen and carbon dioxide. The at least one other component, which may be nitrogen, carbon monoxide or methane, constitutes at most 30 mol% of the mixture, preferably at most 20 mol% of the mixture.

The capture of carbon dioxide (CO₂) by a distillation and/or partial condensation process fed by a waste gas from a hydrogen (H₂) production unit comprising a pressure swing adsorption (PSA) hydrogen separation unit is known. The waste gas is depleted in hydrogen relative to the gas feeding this separation unit. The separation unit can be combined with membrane separation of the gas depleted in carbon dioxide produced by the distillation and/or partial condensation process. The aim of this membrane separation is to separate the CO₂ and H₂ from the rest of the gases in two steps. The permeate from a first membrane system is recycled to the PSA, while the permeate from a second membrane system, fed by the residue of the first system, is itself returned to the compression of the feed gas upstream of the separation by distillation and/or by partial condensation in order to be compressed. The residue from the membrane systems is still under pressure.

According to the invention, the waste gas obtained under pressure is expanded in two turbines in series. The cold fluid at the outlet from the two turbines can be sent to the cryogenic process in order to make use of the cold thereof. These two turbines in series can possibly make it possible to drive two boosters in series. These two boosters can make it possible to lower the pressure of the permeate from the first membrane while at the same time being able to recycle it to a PSA which is at a higher pressure. The hot gas at the outlet from the second booster can pass through the heat exchanger in order to exchange the heat thereof.

The use of a turbine booster in cryogenic CO₂ capture processes combined with membranes has already been described in WO2012/064938.

The invention makes it possible to maximize the energy extracted by turbines by taking advantage of the available heat, for example that produced by the boosters. The process is thus more energy efficient because it uses heat, for example that produced by the compression and typically dissipated in cooling water. The invention also makes it possible to obtain higher hydrogen and CO₂ capture yields because it makes it possible to reduce the pressure of the permeate from the first membrane. Lastly, the invention makes it possible to control the risk of the CO₂ freezing at the outlet of turbines.

US2012/121497 describes a process in which the membranes operate at between 50 and 100°C. It is not where the heat comes from for the heat exchanger used, which is incidentally optional.

US2011/138852 describes a process in which a feed flow and a gas formed by partially condensing the feed flow are sent to a cryogenic membrane, after having heated and then cooled the gas to a temperature between 5 and -60°C.

Description of the invention

One subject of the invention provides a process for membrane separation of a mixture containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, comprising the following steps:

- i) heating of the mixture in a heat exchanger up to a first temperature,
- ii) permeation of the heated mixture in a first membrane system, without having cooled the heated mixture or having mixed it with another fluid, making it possible to obtain a first permeate laden with hydrogen and carbon dioxide relative to the mixture and a first residue depleted in hydrogen and carbon dioxide relative to the mixture,
- iii) permeation of the first residue in a second membrane system making it possible to obtain a second permeate laden with hydrogen and carbon dioxide relative to the first residue and a second residue depleted in hydrogen and carbon dioxide relative to the first residue,
- iv) expansion of the second residue at a first pressure in a first turbine in order to obtain a second residue at a second pressure, characterized in that it comprises

v) heating of at least a portion of the second residue at the second pressure up to a second temperature, which may be identical to or different from the first temperature, and

vi) expansion of at least a portion of the second residue heated in step v) at the second temperature in a second turbine from the second pressure down to a third pressure lower than the second pressure.

According to other optional aspects:

- the temperature of the second residue at the first pressure is regulated in order to keep the temperature of the second residue at the second pressure above -80°C , preferably above -60°C , or even above -55°C , in order to avoid the risks of freezing.
- the at least a portion of the second residue is heated according to step v) in the heat exchanger.
- the first permeate is compressed in at least one booster and the boosted first permeate is cooled in the heat exchanger.
- the first permeate is compressed in two boosters in series, of which one booster is coupled to the first turbine and the other booster is coupled to the second turbine.
- the at least a portion of the second residue is heated according to step v) in a heat exchanger other than the heat exchanger in which the mixture is heated.
- at least a portion of the second residue is expanded without having been heated.
- the outlet from the first turbine is at a temperature below 40°C , preferably below -20°C , preferably below -20°C , or even below -40°C .
- the mixture and the at least a portion of the second residue are heated in the heat exchanger starting from the cold end of the latter.
- the at least a portion of the second residue is heated up to between 30 and 80°C .
- the first pressure is between 45 and 60 bara and/or the second pressure is between 15 and 25 bara and/or the third pressure is between 2 and 4.5 bara.
- the permeation of the heated mixture in a first membrane system making it possible to obtain a first permeate depleted in the other more minor compound relative to the mixture and a first residue enriched in the other more minor compound relative to the mixture.
- the permeation of the first residue in a first membrane system making it possible to obtain a second permeate depleted in the other more minor compound relative to

the first residue and a second residue enriched in the other more minor compound relative to the first residue.

Another subject of the invention provides a process for separating a feed gas containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, wherein the feed gas is separated by distillation and/or by partial condensation in an apparatus comprising a heat exchanger, at least one phase separator and/or at least one distillation column in order to form a gaseous mixture and a CO₂-rich fluid, the gaseous mixture is separated by a membrane separation process as described above and the second permeate and/or the residue expanded in the second turbine are sent to the exchanger and/or to the at least one phase separator and/or to the at least one column of the apparatus.

Another subject of the invention provides a process for separating a gas containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, wherein the gas is separated in a PSA in order to form a gas enriched in hydrogen and depleted in carbon dioxide and a feed gas enriched in carbon dioxide and depleted in hydrogen, the feed gas being separated by the process as described above.

Another subject of the invention provides an apparatus for membrane separation of a mixture containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, comprising: a heat exchanger, means for sending a mixture to be heated in a heat exchanger up to a first temperature, a first membrane system, a second membrane system, a first turbine, means for sending only the heated mixture to be separated by permeation in the first membrane system making it possible to obtain a first permeate laden with hydrogen and carbon dioxide relative to the mixture and a first residue depleted in hydrogen and carbon dioxide relative to the mixture, without means for cooling the heated mixture upstream of the first membrane system, means for sending the first residue to be separated by permeation in the second membrane system making it possible to obtain a second permeate laden with hydrogen and carbon dioxide relative to the first residue and a second residue depleted in hydrogen and carbon dioxide relative to the first residue, means for sending the second residue to be expanded down to a first pressure in the first turbine in order to obtain a second residue at a second pressure, characterized in that it comprises:

- i) means for heating at least a portion of the second residue at the second pressure up to a second temperature, which may be identical to or different from the first temperature, and
- ii) a second turbine, means for sending at least a portion of the second residue at the second temperature from the means for heating at least a portion of the second residue to be expanded in the second turbine from the second pressure down to a third pressure lower than the second pressure.

In one embodiment, the invention consists in:

- Heating, in a heat exchanger, for example the one in which the gas to be separated in the first membrane system is heated, the gas exiting the first turbine before carrying out the second expansion in the second turbine. The first pressure at the inlet to the first turbine is preferentially between 45 bara and 60 bar, while the second pressure at the discharge from this first turbine is between 15 bara and 25 bara, depending on the type of machine. The temperature of the gas at the inlet to the first turbine is preferentially between 50°C and 90°C. The gas exiting the first turbine is preferentially at a temperature between -30°C and 40°C. A fraction of this gas (between 15% and 100% depending on the performance sought) is sent to the heat exchanger and/or to the partial condensation and/or distillation unit in order to be heated. This fraction preferably passes through the whole of the exchanger up to the hot end in order preferentially to reach a temperature of between 50°C and 100°C. This makes it possible, after remixing, to obtain temperatures of between 30°C and 100°C at the inlet to the second turbine. At the discharge from the second turbine, the third pressure is preferentially between 2 bara and 4.5 bara.

This arrangement makes it possible to recover more energy at the expansions by having the hottest possible gas at the inlet to the second turbine. No external supply of heat is necessary since the system contains surplus heat. The heat is in this case produced by the boosters.

- Controlling the temperature of the gas at the outlet from the second turbine by virtue of a bypass conduit. The objective is to maintain a sufficient margin with respect to the CO₂ condensation curve and more preferentially with respect to the temperature of the CO₂ triple point. A margin preferentially of more than 1°C is maintained. To control the temperature at the outlet from the second expansion, the temperature at the inlet to this second turbine is regulated. This should be between 30°C and 80°C. In order to regulate this temperature, a portion of the gas at the outlet from the first

turbine is heated through the heat exchanger as described above. The proportions, between hot gas heated up to the hot end of the heat exchanger and cold gas taken directly at the outlet from the first turbine, determine the temperature at the inlet to the second turbine. In order to have the most direct regulation possible, the regulation of the fraction heated in the exchanger is performed directly on the temperature at the outlet from the second turbine.

Two configurations are therefore possible:

- Either it is sought to maximize the energy extracted by the turbines without seeking to make use of the cold created by the turbines. In this case, the fraction sent through the heat exchanger is equal to 100% and the temperature of the gas at the inlet to the second turbine is the hottest temperature obtained by exchange through the heat exchanger, i.e. the temperature of the hot gas exiting the second booster minus the approach in the exchanger. This temperature is preferentially between 50°C and 100°C.
- Or it is sought to maximize the energy extracted by the turbines while desiring to make use of the cold at the outlet from the second turbine in the cryogenic portion of the process. In this case, by using the cold bypass conduit and the temperature regulation, mixing is used to obtain a gas at the inlet to the second turbine at an intermediate temperature (preferentially of between 30°C and 80°C), which makes it possible to obtain a cold temperature at the outlet from the second turbine (preferentially of less than -45°C but greater than -55°C in order to keep a sufficient margin with respect to the triple point of the CO₂ and thus avoid freezing of the CO₂), enabling the use thereof in the cryogenic portion of the process. In fact, the temperature could be lower since the CO₂ is diluted. But if this cold is used against pure CO₂ in the cold portion, there would be a risk of it freezing.

In a variant, it is possible to heat the residue going to the second turbine without passing through the heat exchanger in which the mixture to be separated is heated. Alternatively, the residue may be heated first in the heat exchanger in which the mixture to be separated is heated and then in another exchanger. For this, it is possible to use a dedicated heat exchanger utilizing either heat coming from the SMR or water vapor. This solution makes it possible to achieve even higher temperatures at the inlet to the second turbine. It is also possible, if the hot source allows it, to also heat the residue at the inlet to the first turbine in order to further increase the amount of energy recovered during the expansion.

On the other hand, the first pressure between the two turbines may be chosen such that the temperature at the outlet from the first turbine is cryogenic, i.e. preferentially below -20°C and more preferentially below -40°C . This residue that has been expanded once is therefore sent into the heat exchanger and/or into the partial condensation and/or distillation unit so as to make use of the cold energy. The residue emerges at the hot end of the main exchange line at ambient temperature. The expansion in the second turbine may then be effected in the various ways described above. In order to obtain cryogenic temperatures at the outlet from the two turbines, it is also possible to cool the residue a little before it enters the first turbine.

The invention will be described in greater detail with reference to the figure, in which: [FIG. 1] represents a process according to a variant of the invention.

[FIG. 1] shows a membrane separation process. The gas to be separated is produced by separating, by distillation and/or partial condensation, a feed gas containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen. This feed gas is a waste gas from a PSA producing hydrogen from a synthesis gas produced by a reformer, for example by steam reforming (SMR).

The gas mixture 1 may be a gas from a phase separator of a partial condensation process and/or a top gas from a distillation column, the phase separator and/or column forming part of an apparatus operating below 0°C to separate the feed gas.

The gas mixture 1 containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen. A mixture containing predominantly hydrogen and carbon dioxide has a composition such that at least 50 mol% of the mixture is composed of hydrogen and carbon dioxide. This mixture 1 is heated in a heat exchanger E, passing from the hot end to the cold end, and is separated in a first membrane system M1 to form a first permeate P1 and a first residue R1. The first permeate P1 is sent at least in part to be cooled in the heat exchanger E and is then compressed in two boosters in series C2, C1 and the boosted first permeate is sent to be cooled in the heat exchanger E before being sent as feed gas to the PSA in order to recover the hydrogen contained therein.

A portion B3 of the first permeate P1 may bypass the exchanger E and be sent directly from the membrane system M1 without having been cooled, the valve V3 being open. Likewise, a portion B2 of the boosted first permeate may bypass the exchanger E and be sent directly to the PSA without having been cooled, the valve V2 being open.

In both cases, this makes it possible to regulate the temperature of the fluid 3 and, by extension, that of the permeate P1 and of the residue R1.

The first residue R1 coming from the first membrane system M1 is separated in the second membrane system M2, forming a second permeate P2 and a second residue R2. The second permeate P2 is cooled in the heat exchanger E and is separated in an apparatus for separation by partial condensation and/or distillation, which produces the mixture 1. The second residue R2 exits the second membrane system M2 at between 45 and 60 bara and between 50 and 90°C. It is then expanded in a first turbine T1 to form a flow at between 15 and 25 bara. The temperature of the expanded first residue does not exceed 40°C, and preferably is below 0°C, or else below -20°C, or even below -40°C. The expanded second residue is sent at least in part to be heated in the exchanger E by being sent to the cold end in order to exit at the hot end at a temperature between 50 and 100°C. Between 15% and 100% of the expanded second residue at the first temperature is heated in the exchanger E. A portion may bypass the exchanger E and rejoin the rest of the expanded second residue via a bypass conduit B1 without having been heated, the valve V1 being open. In this way, it is possible to regulate the temperature of the gas sent to the second turbine T2, such that it varies between 30 and 100°C. The gas expanded in the turbine T2 is at between 2 and 4.5 bara and at a temperature preferably below -45°C but above -55°C and is sent to supply cold to the separation by partial condensation and/or distillation. This gas R2 expanded in the two turbines T1, T2 may be used to regenerate the dryers upstream of the cold separation.

The permeation of the heated mixture 1 in the first membrane system M1 makes it possible to obtain a first permeate P1 depleted in the other more minor compound relative to the mixture and a first residue R1 enriched in the other more minor compound relative to the mixture.

The permeation of the first residue R1 in the second membrane system M2 makes it possible to obtain a second permeate P2 depleted in the other more minor compound relative to the first residue and a second residue R2 enriched in the other more minor compound relative to the first residue.

Claims

1. A process for membrane separation of a mixture (1) containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, comprising the following steps:
 - i) heating of the mixture in a heat exchanger (E) up to a first temperature,
 - ii) permeation of the heated mixture in a first membrane system (M1), without having cooled the heated mixture or having mixed it with another fluid, making it possible to obtain a first permeate (P1) laden with hydrogen and carbon dioxide relative to the mixture and a first residue (R1) depleted in hydrogen and carbon dioxide relative to the mixture,
 - iii) permeation of the first residue in a second membrane system (M2) making it possible to obtain a second permeate (P2) laden with hydrogen and carbon dioxide relative to the first residue and a second residue (R2) depleted in hydrogen and carbon dioxide relative to the first residue,
 - iv) expansion of the second residue at a first pressure in a first turbine (T1) in order to obtain a second residue at a second pressure, characterized in that it comprises
 - v) heating (E) of at least a portion of the second residue at the second pressure up to a second temperature, which may be identical to or different from the first temperature, and
 - vi) expansion of at least a portion of the second residue heated in step v) at the second temperature in a second turbine (T2) from the second pressure down to a third pressure lower than the second pressure.
2. The process as claimed in claim 1, wherein the temperature of the second residue (R2) at the first pressure is regulated in order to keep the temperature of the second residue at the second pressure above -80°C, preferably above -60°C, or even above -55°C, in order to avoid the risks of freezing.
3. The process as claimed in claim 1 or 2, wherein the at least a portion of the second residue (R2) is heated according to step v) in the heat exchanger.
4. The process as claimed in claim 3, wherein the first permeate (P1) is compressed in at least one booster (C1, C2) and the boosted first permeate is cooled in the heat exchanger (E).

5. The process as claimed in one of the preceding claims, wherein the first permeate (P1) is compressed in two boosters in series (C1, C2), of which one booster (C1) is coupled to the first turbine (T1) and the other booster (C2) is coupled to the second turbine (T2).
6. The process as claimed in one of the preceding claims, wherein the at least a portion of the second residue (R2) is heated according to step v) in a heat exchanger other than the heat exchanger (E) in which the mixture is heated.
7. The process as claimed in one of the preceding claims, wherein at least a portion (B1) of the second residue (R2) is expanded without having been heated.
8. The process as claimed in one of the preceding claims, wherein the outlet from the first turbine (T1) is at a temperature below 40°C, preferably below -20°C, preferably below -20°C, or even below -40°C.
9. The process as claimed in one of the preceding claims, wherein the mixture (1) and the at least a portion of the second residue are heated in the heat exchanger (E) starting from the cold end of the latter.
10. The process as claimed in one of the preceding claims, wherein the at least a portion of the second residue (R2) is heated up to between 30 and 80°C.
11. The process as claimed in one of the preceding claims, wherein the first pressure is between 45 and 60 bara and/or the second pressure is between 15 and 25 bara and/or the third pressure is between 2 and 4.5 bara.
12. A process for separating a feed gas containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, wherein the feed gas is separated by distillation and/or by partial condensation in an apparatus comprising a heat exchanger, at least one phase separator and/or at least one distillation column in order to form a gaseous mixture and a CO₂-rich fluid, the gaseous mixture is separated by a membrane separation process as claimed in one of the preceding claims and the second permeate (P2) and/or the residue expanded in the second turbine (T2) are sent to the exchanger and/or to the at least one phase separator and/or to the at least one column of the apparatus.
13. A process for separating a gas containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, wherein the gas is separated in a PSA in order to form a gas enriched in hydrogen and depleted in carbon dioxide and a feed gas enriched in carbon

dioxide and depleted in hydrogen, the feed gas being separated by the process as claimed in claim 12.

14. An apparatus for membrane separation of a mixture (1) containing predominantly hydrogen and carbon dioxide and also at least one more minor compound such as carbon monoxide, methane, nitrogen, comprising: a heat exchanger (E), means for sending a mixture to be heated in the heat exchanger up to a first temperature, a first membrane system (M1), a second membrane system (M2), a first turbine (T1), means for sending only the heated mixture to be separated by permeation in the first membrane system making it possible to obtain a first permeate (P1) laden with hydrogen and carbon dioxide relative to the mixture and a first residue (R1) depleted in hydrogen and carbon dioxide relative to the mixture, without means for cooling the heated mixture upstream of the first membrane system, means for sending the first residue to be separated by permeation in the second membrane system making it possible to obtain a second permeate (P2) laden with hydrogen and carbon dioxide relative to the first residue and a second residue (R2) depleted in hydrogen and carbon dioxide relative to the first residue, means for sending the second residue to be expanded down to a first pressure in the first turbine in order to obtain a second residue at a second pressure, characterized in that it comprises

- i) means (E) for heating at least a portion of the second residue (R2) at the second pressure up to a second temperature, which may be identical to or different from the first temperature, and
- ii) a second turbine (T2), means for sending at least a portion of the second residue (R2) at the second temperature from the means for heating at least a portion of the second residue to be expanded in the second turbine from the second pressure down to a third pressure lower than the second pressure.