

Method and apparatus for separating a gas mixture containing carbon dioxide

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The invention relates to a method and an apparatus for separating a gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide by phase separation and/or by distillation. According to such a method, a gas mixture containing carbon dioxide and at least one lighter impurity (O₂, H₂, CO, etc.),

10 which is for example a boil-off gas from a liquid carbon dioxide storage facility, may be separated to form a liquid depleted in light impurity, which may be returned to the storage facility in liquid form or reused elsewhere in the method. This makes it possible to produce purified carbon dioxide from the vaporization gas coming from the storage facilities in liquid form, the liquid being returned to at least one
15 static or transportable storage facility using loading systems.

Boil-off gases (BOG) are usually generated in the end equipment of a CO₂ separation plant:

- In at least one static CO₂ storage facility, and/or
- In the CO₂ loading systems, and/or
- 20 • During operations to load CO₂ into the transportable storage facilities (for example on ships, tanker trucks, or trains) or into a pipe.

These gases rich in CO₂, generated by several phenomena, are CO₂ losses if they are not recycled or liquefied and returned, since they are usually sent to a vent.

25 With the increased demand for CO₂ capture and separation units and the increased capacity of these units, it has become necessary to process the boil-off gases (BOG) generated.

JP-S-57-149699, published in 1982, describes a distillation method producing liquid CO₂ that is pressurized and sent to a storage facility, the gas in the space
30 above the liquid level in the storage facility being sent to the distillation column.

The preamble of claim 1 has features in common with this document.

In a small-scale CO₂ separation plant, the boil-off gases generated in the storage and loading systems are currently:

- Used for the regeneration of the adsorbent that is used to dry the gas to be liquefied, and then discharged into the atmosphere, or
- Discharged directly into the atmosphere.

The method according to the invention involves recycling the boil-off gas, for example from the storage facilities or the loading systems, to a unit for separating a CO₂ mixture by distillation and/or partial condensation at a suitable location where the conditions (pressure/temperature) are favourable. Furthermore, recycling the boil-off gas to the separation unit increases the demand for coolant liquid. The invention describes the best location for recycling the boil-off gas to optimize the increase of fluid flowing over the liquefactor.

According to one aspect of the subject matter of the invention, it is provided for the boil-off gases to be returned to a phase separator located upstream or downstream of the storage facilities or to another CO₂ separation method.

A distillation column contains means for promoting the exchange of heat and material, such as plates, structured packing, and random-fill packing.

A phase separator does not contain means for promoting the exchange of heat and material, essentially carrying out a separation equivalent to a single theoretical plate.

The refrigeration for the separation may be provided by an open or closed refrigerant cycle containing CO₂. It is also possible to have a cascade arrangement containing another type of compound such as NH₃ or any other refrigerant enabling liquefaction of the CO₂.

According to one aspect of the subject matter of the invention, a method for separating a first gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide is provided, the first gas mixture coming from a liquid carbon dioxide storage facility or being produced when filling a liquid carbon dioxide storage facility, in which the first gas mixture and a second gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide are separated in a separation system comprising a heat exchanger and at least one distillation column to form a liquid flow with a higher carbon dioxide content than the second gas mixture and a gas with a lower carbon dioxide content than the first gas mixture, the second gas mixture is cooled in the heat exchanger upstream of the separation, the liquid flow is withdrawn from a distillation column of the

- separation system, at least a first portion of the liquid flow is sent to at least one liquid carbon dioxide storage facility or even to the liquid carbon dioxide storage facility from where the first gas mixture came, possibly after being pressurized, characterized in that a second portion of the liquid flow is partially vaporized to
- 5 form a two-phase flow and the two-phase flow is separated to form a gas and a liquid in the phase separator, the liquid from the phase separator is vaporized in the heat exchanger to form a vaporized liquid, the gas from the phase separator is heated in the heat exchanger to form a heated gas, a gas is formed by mixing the vaporized liquid and the heated gas and is compressed in a compressor with at
- 10 least a portion of the second mixture, at least partially condensed in the heat exchanger and returned to the column from which the liquid flow was withdrawn and the first gas mixture is sent directly to the phase separator to be mixed with the two-phase flow, possibly after being expanded.
- 15 According to other optional features:
- the first mixture is expanded upstream of the phase separator,
 - the first gas mixture containing carbon dioxide and at least one impurity is at a temperature below -45°C in a pipe conveying it from the storage facility to the at least one column and/or the at least one phase separator,

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 - the first mixture is separated in a distillation column and a liquid reflux flow constituting a portion of the second mixture is sent to the top of the column,
 - the first mixture comes from a storage facility operating at a pressure greater than the pressure of the column in which the first mixture is separated,
 - the first mixture contains at least 90 mol% of CO_2 , preferably at least 95

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 - mol% of CO_2 , or even at least 97 mol% of CO_2 , or at least 99 mol% of CO_2 ,
 - the second mixture contains at least 20 mol% of CO_2 , preferably at least 40 mol% of CO_2 , or even at least 60 mol% of CO_2 , at least 80 mol% of CO_2 , or at least 90 mol% of CO_2 ,
 - the CO_2 content of the first mixture is at least as high as that of the second

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 - mixture,
 - the at least one impurity lighter than carbon dioxide is nitrogen, oxygen, argon, methane, carbon monoxide or hydrogen,

- the first mixture and/or at least a portion of the second mixture is sent to a column of the system as reboiling gas,
 - an overhead gas of a/the column of the system is heated in the exchanger,
 - all the bottom liquid produced by a/the column of the system is sent to at
 - 5 least one storage facility, which may be transportable,
 - the carbon dioxide content of the liquid flow is higher or lower than the first gas mixture,
 - the first gas mixture contains at least 90 mol% of CO₂, preferably at least 95 mol% of CO₂, or even at least 97 mol% of CO₂, or at least 99 mol% of CO₂,
 - 10 • the second mixture contains at least 20 mol% of CO₂, preferably at least 40 mol% of CO₂, or even at least 60 mol% of CO₂, at least 80 mol% of CO₂, or at least 90 mol% of CO₂,
 - the carbon dioxide content of the first mixture is at least as high as that of the second mixture,
 - 15 • the at least one impurity lighter than carbon dioxide is nitrogen, oxygen, argon, methane, carbon monoxide, hydrogen or helium,
 - the phase separator operates at a pressure below the pressure of the storage facility,
 - the phase separator operates at approximately 5.6 bara,
 - 20 • the storage facility operates or the filling is carried out at between 6 and 12 bara, or even between 6 and 8 bara,
 - an overhead gas of a column of the system or of the column of the system is heated in the exchanger.
- 25 According to another aspect of the subject matter of the invention, an apparatus for separating a first gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide is provided, comprising means for conveying the first gas mixture from a liquid carbon dioxide storage facility or a filling pipe of a liquid carbon dioxide storage facility, a separation system comprising a heat
- 30 exchanger and at least one phase separator and at least one distillation column, means for sending the first gas mixture to be separated in the separation system, means for sending a second gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide to be cooled or even condensed in the

heat exchanger, means for conveying the second mixture cooled in the heat exchanger to be separated in the at least one distillation column to form a liquid flow with a higher carbon dioxide content than the second gas mixture and a gas with a lower carbon dioxide content than the second gas mixture, means for
 5 withdrawing the liquid flow from a distillation column of the separation system, possibly a pump for pressurizing at least a first portion of the liquid flow, means for sending the at least one first portion of the liquid flow to a liquid carbon dioxide storage facility or even to the liquid carbon dioxide storage facility from where the first gas mixture came, characterized in that it comprises means for partially
 10 vaporizing a second portion of the liquid flow to form a two-phase flow, means for sending the two-phase flow to the phase separator to form a gas and a liquid, means for sending the liquid from the phase separator to be vaporized in the heat exchanger to form a vaporized liquid, means for sending the gas from the phase separator to be heated in the heat exchanger to form a heated gas, means for
 15 forming a gas by mixing the vaporized liquid and the heated gas, a compressor, means for sending the gas formed by mixing the liquid and the gas and at least a portion of the second gas mixture to the compressor, means for sending the gas compressed in the compressor to the heat exchanger, means for sending the partially-condensed compressed gas to the at least one phase separator of the
 20 system or to the column from which the liquid flow was withdrawn, and means for sending the first mixture to the phase separator to be mixed with the two-phase flow.

The apparatus may comprise means for expanding the first gas mixture upstream of the phase separator.

25 The invention will be described in greater detail with reference to the figure, in which:

[FIG.1] represents a method according to the invention.

In Figure 1, the apparatus for separating the first gas mixture 05 comprising CO₂ and at least one impurity lighter than CO₂, such as helium, methane, carbon
 30 monoxide, hydrogen, nitrogen, argon or oxygen, comprises a heat exchanger 20 and a distillation column 40.

The source 70 of the first gas mixture 05 may be:

- at least one static storage facility for storing liquid CO₂ in which a boil-off gas 05 is generated by the heat absorption, and/or
- at least one liquid CO₂ loading system connected to a storage facility producing a boil-off gas 05, and/or
- 5 • at least one transportable storage facility (for example on ships/tanker trucks/trains), at least a portion of the first gas mixture 05 being generated during liquid CO₂ loading operations.

The gas source 70 may be supplied exclusively with liquid CO₂ by the apparatus in Figure 1, exclusively by at least one other liquid CO₂ production apparatus, or by
10 both.

In this case, the bottom of the column 40 is heated by a flow of reboiling gas 07, which is a second gas mixture cooled in the heat exchanger 20. In a variant, a CO₂-rich gas 07 may be formed by vaporizing a portion of the bottom liquid from the column 40 in the exchanger 20 and returning it to the column. Other sources of
15 reboiling gas may be used.

The first gas mixture 05 contains at least 90 mol% of CO₂, preferably at least 95 mol% of CO₂, or even at least 97 mol% of CO₂, or at least 99 mol% of CO₂.

The second mixture 07, 11 contains at least 20 mol% of CO₂, preferably at least 40 mol% of CO₂, or even at least 60 mol% of CO₂, at least 80 mol% of CO₂, or at
20 least 90 mol% of CO₂.

The carbon dioxide content of the first mixture 05 is at least as high as the second mixture 07, 11, 12.

Liquid formed in the bottom of the column 40 is withdrawn from the column and split into two portions. This liquid has a higher carbon dioxide content than the
25 second gas mixture 11 and possibly a higher CO₂ content than the first gas mixture 05. Conversely, it may have a lower CO₂ content than the first gas mixture 05. A first portion 33 is pressurized by a pump P and either sent directly to a storage facility 70, which may be the source of the gas 05, or another storage facility, or processed to form a liquid to be sent to the gas source 70 or to another
30 storage facility.

A second portion 03 of the bottom liquid is expanded to partially vaporize it, forming a two-phase flow. The two-phase flow is sent to a drum 50 acting as a phase separator. The gas and the liquid formed in the drum acting as phase

separator are sent to the heat exchanger (in order to provide the required refrigeration energy) where the liquid is vaporized to form a gas, this gas and the gas from the separator 50 heated in the heat exchanger being mixed to form a gas 01. In both cases, the gas 01 is compressed in a compressor 10 to form a compressed gas that is then cooled in the heat exchanger 20, then expanded in a valve to be sent as a liquid 2 to an intermediate level of the column 40.

A gas 11 containing carbon dioxide and at least one impurity lighter than carbon dioxide is sent to the inlet of the compressor or to an intermediate level of the compressor to be compressed. This gas constitutes the second gas mixture.

- Future developments in CO₂ transportation are expected to include storing and loading systems operating at low pressure. Storage or loading pressure may vary between 6 bara and 12 bara (or from 6 bara to 8 bara). In this case, the gas 05 is usually at approximately -52°C. Under these conditions, the pressure of the gas 05 is lower than the pressure in the phase separator or the column 40. As shown in Figure 1, the gas 05 coming from the source 70 is then expanded through the valve 60 to form a two-phase flow and sent to the drum 50 (usually operating at a pressure below the pressure of the storage facility 70, or generally at approximately 5.6 bara). No portion of the first gas mixture 05 is sent directly to the column 40. Thus, the first gas mixture 05 is sent to be separated in the column 40, but after being mixed with the fluids produced by expanding the second portion 03 of the bottom liquid from the column 40 and with a portion of the second mixture 11. This arrangement may also be suitable where the light-impurity content of the first mixture 05 is so high that it has to be mixed with a fluid richer in CO₂ in order to be processed.
- Insulation is provided for the pipe for the gas 05 so that said gas is not heated between the source 70 and the separation apparatus, since the source 70 operates at a below-ambient temperature.

Brief Description of the Drawings

- Fig. 1** is a schematic diagram of an apparatus for performing the method for separating a gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide, as described herein.

Claims

- 5 1. Method for separating a first gas mixture (05) containing carbon dioxide and at least one impurity lighter than carbon dioxide, the first gas mixture coming from a liquid carbon dioxide storage facility (70) or being produced when filling a liquid carbon dioxide storage facility, in which the first gas mixture and a second gas mixture (11) containing carbon dioxide and at least one impurity lighter than
10 carbon dioxide are separated in a separation system comprising a heat exchanger (20) and at least one distillation column (40) to form a liquid flow with a higher carbon dioxide content than the second gas mixture and a gas (45) with a lower carbon dioxide content than the first gas mixture, the second gas mixture is cooled in the heat exchanger upstream of the separation, the liquid flow is withdrawn from
15 a distillation column of the separation system, at least a first portion (33) of the liquid flow is sent to at least one liquid carbon dioxide storage facility (70) or even to the liquid carbon dioxide storage facility from where the first gas mixture came, possibly after being pressurized, characterized in that a second portion (03) of the liquid flow is partially vaporized to form a two-phase flow and the two-phase flow is
20 separated to form a gas and a liquid in the phase separator (50), the liquid from the phase separator is vaporized in the heat exchanger to form a vaporized liquid, the gas from the phase separator is heated in the heat exchanger to form a heated gas, a gas (01) is formed by mixing the vaporized liquid and the heated gas and is compressed in a compressor (10) with at least a portion (11) of the second
25 mixture, at least partially condensed in the heat exchanger and returned to the column (40) from which the liquid flow was withdrawn and the first gas mixture (05) is sent directly to the phase separator (50) to be mixed with the two-phase flow, possibly after being expanded.
2. Method according to Claim 1, in which the first gas mixture (05) comes from
30 the storage facility at a pressure below the pressure of the column (40).
3. Method according to Claim 1, in which the first mixture (05) comes from a storage facility (70) operating at a pressure greater than the pressure of the column (40) in which the first mixture is separated.

4. Method according to one of the preceding claims, in which the first gas mixture (05) containing carbon dioxide and at least one impurity is at a temperature below -45°C in a pipe conveying it from the storage facility (70) to the at least one column (40) and/or the at least one phase separator.
- 5 5. Method according to one of the preceding claims, in which the first gas mixture contains at least 90 mol% of CO_2 , preferably at least 95 mol% of CO_2 , or even at least 97 mol% of CO_2 , or at least 99 mol% of CO_2 .
6. Method according to one of the preceding claims, in which the second mixture contains at least 20 mol% of CO_2 , preferably at least 40 mol% of CO_2 , or
10 even at least 60 mol% of CO_2 , at least 80 mol% of CO_2 , or at least 90 mol% of CO_2 .
7. Method according to one of the preceding claims, in which the CO_2 content of the first mixture is at least as high as that of the second mixture.
8. Method according to one of the preceding claims, in which the at least one
15 impurity lighter than carbon dioxide is nitrogen, oxygen, argon, methane, carbon monoxide or hydrogen.
9. Method according to one of the preceding claims, in which the phase separator (50) operates at a pressure below the pressure of the storage facility (70).
- 20 10. Method according to the preceding claim, in which the phase separator (50) operates at approximately 5.6 bara.
11. Method according to one of the preceding claims, in which the storage facility (70) operates or the filling is carried out at between 6 and 12 bara, or even between 6 and 8 bara.
- 25 12. Method according to one of the preceding claims, in which an overhead gas (45) of a column of the system or of the column of the system is heated in the exchanger (20).
13. Apparatus for separating a first gas mixture containing carbon dioxide and at least one impurity lighter than carbon dioxide, comprising means for conveying
30 the first gas mixture (05) from a liquid carbon dioxide storage facility (70) or a filling pipe of a liquid carbon dioxide storage facility, a separation system (40, 50) comprising a heat exchanger (20) and at least one phase separator (50) and at least one distillation column (40), means for sending the first gas mixture to be

separated in the separation system, means for sending a second gas mixture (11, 12) containing carbon dioxide and at least one impurity lighter than carbon dioxide to be cooled or even condensed in the heat exchanger, means for conveying the second mixture cooled in the heat exchanger to be separated in the at least one
5 distillation column to form a liquid flow with a higher carbon dioxide content than the second gas mixture and a gas with a lower carbon dioxide content than the second gas mixture, means for withdrawing the liquid flow from a distillation column of the separation system, possibly a pump (P) for pressurizing at least a first portion (33) of the liquid flow, means for sending the at least one first portion
10 of the liquid flow to a liquid carbon dioxide storage facility (70) or even to the liquid carbon dioxide storage facility from where the first gas mixture came, characterized in that it comprises means for partially vaporizing a second portion of the liquid flow (03) to form a two-phase flow, means for sending the two-phase flow to the phase separator (50) to form a gas and a liquid, means for sending the
15 liquid from the phase separator to be vaporized in the heat exchanger to form a vaporized liquid, means for sending the gas from the phase separator to be heated in the heat exchanger to form a heated gas, means for forming a gas by mixing the vaporized liquid and the heated gas, a compressor (10), means for sending the gas formed by mixing the liquid and the gas and at least a portion (11) of the
20 second gas mixture to the compressor, means for sending the gas compressed in the compressor to the heat exchanger, means for sending the partially-condensed compressed gas to the at least one phase separator (40') of the system or to the column (40) from which the liquid flow was withdrawn, and means for sending the first mixture to the phase separator (50) to be mixed with the two-phase flow.

25 14. Apparatus according to Claim 13, comprising means (60) for expanding the first gas mixture (05) upstream of the phase separator (50).