METHOD FOR TREATING A HYDROCARBON STREAM

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Abstract

The present invention relates to a method for treating a natural gas feed stream, containing >10 mole % CO2, the method at least comprising the steps of separating the feed stream (10) in a first (2) or a second (3) gas/liquid separator, removing from the top of the second gas/liquid separator (3) a gaseous stream (60), partially condensing it by heat exchanging against a cold stream (120) and feeding it (70) into a third gas/liquid separator (4) thereby obtaining a liquid stream (80) and a gaseous stream (90) and feeding the liquid stream (80) having a temperature above the freezing point of CO2 at the prevailing conditions, into the second gas/liquid separator (3) removing from the bottom of the second gas/liquid separator (3) a liquid stream (100, 100a).
METHOD FOR TREATING A HYDROCARBON STREAM

[0001] The present invention relates to a method of treating a hydrocarbon stream such as a natural gas stream, containing >10 mole % CO₂.

[0002] In particular the present invention relates to the treatment of a natural gas stream, containing >10 mole % CO₂, involving recovery of at least some of the propane, butanes and higher hydrocarbons such as pentane from the natural gas. The recovery of hydrocarbons may be done for several purposes. One purpose may be the production of hydrocarbon streams consisting primarily of hydrocarbons heavier than methane such as natural gas liquids (NGLs; usually composed of ethane, propane and butanes), liquefied petroleum gas (LPG; usually composed of propane and butane) or condensates (usually composed of butanes and heavier hydrocarbon components). Another purpose may be the adjustment of e.g. the heating value of the hydrocarbon stream to correspond to desired specifications.

[0003] Several processes and apparatuses for treating a hydrocarbon stream are known. An example is given in US 2005/0268469 A1 relating to a process for processing natural gas or other methane-rich gas streams to produce a liquefied natural gas (LNG) stream that has a high methane purity and a liquid stream containing predominantly hydrocarbons heavier than methane.

[0004] A problem of the known method is that it cannot properly treat hydrocarbon streams containing relatively high CO₂ concentrations.

[0005] A further problem of the known method is that it is rather complicated thereby resulting in high capital expenses (CAPEX), but at the same time it does not obtain a satisfactory recovery of in particular propane.

[0006] Other examples of such processes are described in U.S. Pat. No. 5,960,644 and in “LPG-recovery processes for baseload LNG plants examined”, Chen-Hwa Chiu, Oil & Gas Journal Nov. 24, 1997. Again, a problem of these known methods is that they cannot properly treat hydrocarbon streams containing relatively high CO₂ concentrations.

[0007] It is an object of the present invention to minimize one or more of the above problems, while at the same time maintaining or even improving the recovery of ethane and heavier hydrocarbons, in particular propane, from the hydrocarbon stream.

[0008] It is a further object of the present invention to provide an alternative method for treating a hydrocarbon stream, in particular a natural gas stream, having a high CO₂ concentration.

[0009] One or more of the above or other objects are achieved according to the present invention by providing a method of treating a hydrocarbon stream such as a natural gas stream, containing >10 mole % CO₂, the method at least comprising the steps of:

[0010] (a) supplying a partly condensed feed stream, containing >10 mole % CO₂, to a first gas/liquid separator;

[0011] (b) separating the feed stream in the first gas/liquid separator into a gaseous stream and a liquid stream;

[0012] (c) expanding the liquid stream obtained in step (b) and feeding it into a second gas/liquid separator at a first feeding point;

[0013] (d) expanding the gaseous stream obtained in step (b), thereby obtaining an at least partially condensed stream, and subsequently feeding it into the second gas/liquid separator at a second feeding point, the second feeding point being at a higher level than the first feeding point;

[0014] (e) removing from the top of the second gas/liquid separator a gaseous stream, partially condensing it and feeding it into a third gas/liquid separator;

[0015] (f) separating the stream fed in the third gas/liquid separator in step (e) thereby obtaining a liquid stream and a gaseous stream;

[0016] (g) feeding the liquid stream obtained in step (f), having a temperature above the freezing point of CO₂ at the prevailing conditions, into the second gas/liquid separator at a third feeding point, the third feeding point being at a higher level than the second feeding point; and

[0017] (h) removing from the bottom of the second gas/liquid separator a liquid stream;

[0018] wherein the gaseous stream removed from the second gas/liquid separator in step (e) is partially condensed by heat exchanging against a cold stream.

[0019] It has been found that using the surprisingly simple method according to the present invention for treating a hydrocarbon stream such as a natural gas stream, containing >10 mole % CO₂, the CAPEX can be significantly lowered. Further, also due to its simplicity, the method according to the present invention and apparatuses for performing the method have proven very robust when compared with known line-ups.

[0020] Furthermore it has been found that according to the present invention a higher propane recovery can be obtained thereby resulting in a leaner methane-rich natural gas stream (that may be liquefied subsequently, if desired). The method according to the present invention has also been proven suitable for feed streams having a pressure well below 70 bar, at the same time keeping up a relatively high propane recovery.

[0021] Whenever in the specification and claims reference is made to a pressure in bar, this is a pressure in bar (absolute).

[0022] The hydrocarbon stream may be any suitable gas stream to be treated, but is usually a natural gas stream obtained from natural gas or petroleum reservoirs. As an alternative the natural gas stream may also be obtained from another source, also including a synthetic source such as a Fischer-Tropsch process.

[0023] Usually the natural gas stream is comprised substantially of methane. Preferably the feed stream comprises at least 60 mol % methane.

[0024] Depending on the source, the natural gas may contain varying amounts of hydrocarbons heavier than methane such as ethane, propane, butanes and pentanes as well as some aromatic hydrocarbons. The natural gas stream may, besides CO₂, also contain non-hydrocarbons such as H₂O, N₂, mercury, H₂S and other sulphur compounds.

[0025] If desired, the feed stream containing the natural gas may be pre-treated before feeding it to the first gas/liquid separator. This pre-treatment may comprise removal of undesired components such as H₂O, mercury, H₂S and other sulphur compounds, or other steps such as pre-cooling, or pre-pressurizing. As these steps are well known to the person skilled in the art, they are not further discussed here.

[0026] The first, second and third gas/liquid separator may be any suitable means for obtaining a gaseous stream and a liquid stream, such as a scrubber, distillation column, etc. If desired, four or more gas/liquid separators may be present.

[0027] Also, the person skilled in the art will understand that the steps of expanding may be performed in various ways.
using any expansion device (e.g. using a throttling valve, a flash valve or a common expander).

[0028] The person skilled in the art will readily understand that treated hydrocarbon streams may be further processed, if desired. Also, further intermediate processing steps between the first and third gas/liquid separator may be performed.

[0029] According to a preferred embodiment of the present invention the second gas/liquid separator is a distillation column. Accordingly, according to a preferred embodiment, the invention relates to a method of treating a hydrocarbon stream such as a natural gas stream, containing >10 mole % CO₂, the method at least comprising the steps of:

[0030] (a) supplying a partly condensed feed stream (10) containing >10 mole % CO₂ to a first gas/liquid separator (2);

[0031] (b) separating the feed stream (10) in the first gas/liquid separator (2) into a gaseous stream (20) and a liquid stream (30);

[0032] (c) expanding the liquid stream (30) obtained in step (b) and feeding it (40) into a distillation column (3) at a first feeding point (31);

[0033] (d) expanding the gaseous stream (20) obtained in step (b), thereby obtaining an at least partially condensed stream (50), and subsequently feeding it into the distillation column (3) at a second feeding point (32), the second feeding point (32) being at a higher level than the first feeding point (31);

[0034] (e) removing from the top of the distillation column (3) a gaseous stream (60), partially condensing it and feeding it (70) into a third gas/liquid separator (4);

[0035] (f) separating the stream (70) fed in the third gas/liquid separator (4) in step (e) thereby obtaining a liquid stream (80) and a gaseous stream (90);

[0036] (g) feeding the liquid stream (80) obtained in step (f), having a temperature above the freezing point of CO₂ at the prevailing conditions, into the distillation column (3) at a third feeding point (33), the third feeding point (33) being at a higher level than the second feeding point (32); and

[0037] (h) removing from the bottom of the distillation column (3) a liquid stream (100, 10a);

[0038] wherein the gaseous stream (60) removed from the distillation column (3) in step (e) is partially condensed by heat exchanging against a cold stream (120).

[0039] When the distillation column is provided with distillation trays, a distillation stage corresponds to one distillation tray, and when the column is provided with packing (random or structured) a distillation stage corresponds to a theoretical stage.

[0040] Where in the specification and in the claims a level of introducing a stream into the distillation column is defined relative to introducing another stream, there is at least one distillation stage between the two levels, the same applies to defining the level of removing a stream from the distillation column. The top of the distillation column is that part of the distillation column that is located above the uppermost distillation stage, and the bottom of the column is that part of the distillation column that is located below the lowermost distillation stage.

[0041] According to another preferred embodiment of the present invention the cold stream is selected such that the partially condensed stream obtained in step (c) has a temperature above the freezing point of CO₂ at the prevailing conditions, preferably greater than or equal to -60°C., more preferably a temperature from -60°C. to -40°C., even more preferably a temperature from -60°C. to -50°C., in particular from -55°C. to -50°C.

[0042] Further it is preferred that the temperature of the liquid stream obtained in step (f) is preferably greater than or equal to -60°C., more preferably a temperature from -60°C. to -40°C., even more preferably a temperature from -60°C. to -45°C., even more preferably a temperature from -60°C. to -50°C., in particular from -35°C. to -50°C. near the third feeding point.

[0043] The person skilled in the art will readily understand that the freezing point of CO₂ at the prevailing conditions may vary dependent on the prevailing pressure.

[0044] According to a particularly preferred embodiment the cold stream is obtained from a separate source of liquefied natural gas (LNG), preferably from an LNG storage tank, more preferably located at an LNG import terminal. With 'separate source' for the cold stream is meant that preferably no cold stream is used that is generated during the treating itself or downstream of the treating.

[0045] Further it is preferred that >75% by weight of the propane present in the partially condensed feed stream is recovered in the liquid stream obtained in step (h), preferably >80, more preferably >85, even more preferably >90, most preferably >95% by weight.

[0046] Also it is preferred that the partially condensed feed stream contains >15 mole % CO₂ and preferably <70 mole % CO₂, more preferably <50 mole % CO₂, even more preferably <25 mole % CO₂.

[0047] Furthermore the partially condensed feed stream preferably has a pressure >20 bar, more preferably from 30 to 100 bar, even more preferably from 38 to 70 bar.

[0048] Further it is preferred that the pressure in the second gas/liquid separator is from 10 to 50 bar, preferably from 30 to 40 bar, more preferably from 30 to 37 bar, even more preferably from 33 to 36 bar, in particular about 35 bar.

[0049] Typically, the pressure of any feed stream to the second gas/liquid separator is in the range from 0 to 5 bar higher than the pressure in the second gas/liquid separator, preferably from 0 to 2 bar higher, even more preferably from 0 to 1 bar higher, in particular substantially the same pressure.

[0050] Although the gaseous stream obtained in step (f) may be used for various purposes it is preferably sent to a gas network. Alternatively, it may e.g. be liquefied thereby obtaining a liquefied hydrocarbon stream such as liquefied natural gas (LNG). Typically, the CO₂ concentration in the gaseous stream obtained in step (f) is so low (e.g. less than 50 ppmv) that the CO₂ will not freeze at the lower temperature encountered in liquefaction of the gaseous stream obtained in step (f).

[0051] Further, the liquid stream removed from the bottom of the second gas/liquid separator is preferably subjected to distillation thereby obtaining two or more distilled streams.

[0052] In a special embodiment the partially condensed feed stream has been previously cooled against a cold stream, preferably against a cold stream that has been obtained from a separate source of a liquefied hydrocarbon stream, in particular LNG, preferably obtained from an LNG storage tank, more preferably located at an LNG import terminal.

[0053] Hereinafter the invention will be further illustrated by the following non-limiting drawing.

[0054] FIG. 1 schematically depicts a process scheme in accordance with the present invention.
For the purpose of this description, a single reference number will be assigned to a line as well as to a stream that carries a line. For the purpose of this description, a single reference number will be assigned to a line as well as to a stream that carries a line. The purpose of this description is to explain the proper function of this invention. The process scheme of FIG. 1 comprises a first gas/liquid separator 2, a second gas/liquid separator 3 (in the form of a distillation column), a third gas/liquid separator 4, a first expander 6, a second expander 7 (in the form of a throttling valve), a first heat exchanger 8, a separate source 13 of a cold stream (in the embodiment of FIG. 1 an LNG storage tank at an LNG import terminal), a gas network 14 and a distillation unit 15. The person skilled in the art will readily understand that further elements may be present if desired.

During use, a partly condensed feed stream 10 containing natural gas is supplied to the inlet 21 of the first gas/liquid separator 2 at a certain inlet pressure and inlet temperature. Typically, the inlet pressure to the first gas/liquid separator 2 will be between 10 and 100 bar, preferably at or above 30 bar, more preferably at or above 38 bar and preferably below 90 bar, more preferably at or below 70 bar. The temperature will usually be between 0°C and 60°C. To obtain the partly condensed feed stream 10, it may have been pre-cooled in several ways. In the embodiment of FIG. 1, the feed stream 10 has been heated exchanged in heat exchanger 11 against stream 9 to be discussed hereafter and subsequently in heat exchanger 5 against stream 130 originating from the LNG storage tank 13. It goes without saying that instead of stream 130 a common external refrigerant such as propane or another cooler such as an air or water cooler may be used.

If desired the feed stream 10 may have been previously treated before it is fed to the first gas/liquid separator 2. As an example, CO₂, H₂S and hydrocarbon components having the molecular weight of pentane or higher may also at least partially be removed from the feed stream 10 before entering the first separator 2.

In the first gas/liquid separator 2, the feed stream 10 (fed at inlet 21) is separated into a gaseous overhead stream 20 (removed at first outlet 22) and a liquid bottom stream 30 (removed at second outlet 23). The overhead stream 20 is enriched in methane (and usually also ethane) relative to the feed stream 10.

The bottom stream 30 is generally liquid and usually contains some components that are freezeable when they would be brought to a temperature at which methane is liquefied. The bottom stream 30 may also contain hydrocarbons that can be separately processed to form liquefied petroleum gas (LPG) products. The stream 30 is expanded in the second expander 7 to the operating pressure of the distillation column 3 (usually about 35 bar) and fed into the same at the first feeding point 31 as stream 40. If desired a further heat exchanger (not shown) may be present on line 40 to heat the stream 40. The second expander 7 may be any expansion device such as a common expander as well as a flash valve.

The gaseous overhead stream 20 removed at the first outlet 22 of the first separator 2 is at least partially condensed in the first expander 6 and subsequently fed as stream 50 into the distillation column 3 at a second feeding point 32, the second feeding point 32 being at a higher level than the first feeding point 31. If desired a further heat-exchanging step may take place between the first expander 6 and the second feeding point 32.

If desired (as indicated by dashed lines in FIG. 1) the gaseous overhead stream 20 may be split into two streams; the "additional" stream 20a may be expanded in expander 6a and fed into the distillation column 3 at a further feeding point 37.

Preferably, the pressure in the distillation column 3 is from 10 to 50 bar, preferably from 30 to 40 bar, more preferably from 30 to 37 bar, even more preferably from 33 to 36 bar, in particular about 35 bar.

From the top of the distillation column 3, at first outlet 34, a gaseous overhead stream 60 is removed that is partially condensed in first heat exchanger 8 while heat exchanging it against cold stream 120 (originating from LNG storage tank 13) and is fed into third gas/liquid separator 4 (at inlet 41) as stream 70.

Preferably the amount, flow rate and temperature of the cold stream 120 are selected such that the partially condensed stream 70 has a temperature greater than or equal to −60°C, more preferably from −60°C to −40°C, even more preferably a temperature from −60°C to −45°C, even more preferably a temperature from −60°C to −50°C, in particular from −55°C to −50°C.

The stream 70 being fed into the third gas/liquid separator 4 at inlet 41 is separated thereby obtaining a gaseous stream 90 (at outlet 42) and a liquid stream 80 (at outlet 43).

The liquid stream 80 removed at outlet 43 is pumped via pump 9 and fed into the distillation column 3 at a third feeding point 33, the third feeding point 33 being at a higher level than the second feeding point 32. Preferably the third feeding point 33 is at the top of the distillation column 3.

Preferably, the temperature of the liquid stream 80 is at or above −60°C near the third feeding point 33, more preferably a temperature from −60°C to −40°C, even more preferably a temperature from −60°C to −45°C, even more preferably a temperature from −60°C to −50°C, in particular from −55°C to −50°C near the third feeding point 33. Herewith it is prevented that the CO₂ freezes and blocks the system, while at the same time a high recovery of propane may be obtained in the distillation column 3.

The gaseous stream 90 obtained at the outlet 42 of the third gas/liquid separator 4 is forwarded to the gas network 14 after heat exchanging against the feed stream 10 in heat exchanger 11 and optionally compressing in compressor 12 (which is functionally coupled to first expander 6).

Usually, a liquid bottom stream 100 is removed from the second outlet 35 of the distillation column 3 and is subjected to one or more distillation steps in a distillation unit 15 to collect various natural gas liquid products. As the person skilled in the art knows how to perform distillation steps, this is not further discussed here.

If desired, as shown in FIG. 1, a part of the liquid bottom stream 100 may be returned to the bottom of the distillation column 3 as stream 110, the remainder of stream 100 being indicated with stream 100a.

Table 1 gives an overview of the pressures and temperatures of a stream at various points in the example of FIG. 1. Also the mole % of propane is indicated. The feed stream in line 10 of FIG. 1 comprised approximately the following composition: 64% methane, 8% ethane, 4% propane, 2% butanes and pentane, 20% CO₂ and 2% N₂. Other components such as H₂S and H₂O were previously removed.
<table>
<thead>
<tr>
<th>Line</th>
<th>Pressure (bar)</th>
<th>Temperature (°C.)</th>
<th>Mole % propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>39.3</td>
<td>-10</td>
<td>4.5</td>
</tr>
<tr>
<td>20</td>
<td>39.2</td>
<td>-10</td>
<td>3.8</td>
</tr>
<tr>
<td>30</td>
<td>39.2</td>
<td>-10</td>
<td>20.5</td>
</tr>
<tr>
<td>40</td>
<td>35.0</td>
<td>-12</td>
<td>20.5</td>
</tr>
<tr>
<td>50</td>
<td>35.0</td>
<td>-16</td>
<td>3.8</td>
</tr>
<tr>
<td>60</td>
<td>35.0</td>
<td>-19</td>
<td>0.2</td>
</tr>
<tr>
<td>70</td>
<td>35.0</td>
<td>-50</td>
<td>0.2</td>
</tr>
<tr>
<td>80</td>
<td>35.0</td>
<td>-50</td>
<td>0.6</td>
</tr>
<tr>
<td>90</td>
<td>35.0</td>
<td>-50</td>
<td>0.01</td>
</tr>
<tr>
<td>100</td>
<td>34.8</td>
<td>50</td>
<td>60.7</td>
</tr>
</tbody>
</table>

**TABLE I**

**TABLE II**

<table>
<thead>
<tr>
<th>Component</th>
<th>Molar fraction of stream 10 in FIG. 1</th>
<th>Molar fraction of stream 100a in FIG. 1</th>
<th>Molar fraction of stream 100a in FIG. 1 with a temperature of -30°C for stream 70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (kmol/s)</td>
<td>0.66</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Methane</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.012</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>Propane</td>
<td>0.045</td>
<td>0.012</td>
<td>0.046</td>
</tr>
<tr>
<td>i-Butane</td>
<td>0.148</td>
<td>0.011</td>
<td>0.123</td>
</tr>
<tr>
<td>Butane</td>
<td>0.125</td>
<td>0.009</td>
<td>0.121</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.041</td>
<td>0.003</td>
<td>0.081</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.032</td>
<td>0.002</td>
<td>0.051</td>
</tr>
<tr>
<td>% Propane recovery</td>
<td>98%</td>
<td>98%</td>
<td>98%</td>
</tr>
</tbody>
</table>

**[0074]** The same line-up as FIG. 1 was used, but instead a higher temperature for stream 70 was used, viz. -30°C. It was found that according to the preferred embodiment of the present invention a significantly higher propane recovery (98%) was obtained in stream 100a, whilst the same line-up with a higher temperature for stream 70 (viz. -30°C) resulted in a propane recovery of only 28%. This is shown in Table II.

2. Method according to claim 1, wherein the cold stream is selected such that the partially condensed stream obtained in step (e) has a temperature above the freezing point of CO₂ at the prevailing conditions.

3. Method according to claim 1, wherein the temperature of the liquid stream obtained in step (f) is at or above -60°C near the third feeding point.

4. Method according to claim 1, wherein the cold stream is selected such that the partially condensed liquid feed stream contains more than 15 mole % CO₂.

5. Method according to claim 1, wherein the cold stream is obtained from a separate source of liquefied natural gas (LNG).

6. Method according to claim 1, wherein the pressure in the second gas/liquid separator is in the range from 10 to 50 bar.

7. Method according to claim 1, wherein the partially condensed feed stream has a pressure above 20 bar.

8. Method according to claim 1, wherein the temperature of the liquid stream obtained in step (f) is at or above -55°C near the third feeding point.

9. Method according to claim 1, wherein the partially condensed feed stream has been previously cooled against a cold stream.

10. Method according to claim 1, wherein the temperature of the liquid stream obtained in step (f) is at or above -50°C near the third feeding point.

11. Method according to claim 1, wherein the liquid stream obtained from the bottom of the second gas/liquid separator is subjected to distillation thereby obtaining two or more distillate streams.

12. Method according to claim 1, wherein the partially condensed feed stream has been previously cooled against a cold stream.

13. Method according to claim 1, wherein the temperature of the liquid stream obtained in step (f) is at or above -55°C near the third feeding point.

14. Method according to claim 1, wherein the cold stream is selected such that the partially condensed stream obtained in step (e) has a temperature from -60°C to -40°C.

15. Method according to claim 1, wherein the cold stream is selected such that the partially condensed stream obtained in step (e) has a temperature greater than or equal to -55°C.
16. Method according to claim 2, wherein the temperature of the liquid stream obtained in step (f) is at or above -60°C near the third feeding point.

17. Method according to claim 2, wherein the cold stream is obtained from a separate source of liquefied natural gas (LNG).

18. Method according to claim 3, wherein the cold stream is obtained from a separate source of liquefied natural gas (LNG).

19. Method according to claim 2, wherein 75% by weight of the propane present in the partially condensed feed stream is recovered in the liquid stream obtained in step (h).

20. Method according to claim 3, wherein 75% by weight of the propane present in the partially condensed feed stream is recovered in the liquid stream obtained in step (h).

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