

## METHOD AND APPLIANCE FOR SEPARATING A SYNTHESIS GAS BY CRYOGENIC DISTILLATION

The present invention relates to a process and to a device for the separation of a synthesis gas by cryogenic distillation.

Synthesis gas contains, as major components, hydrogen, methane and carbon monoxide. It can also contain nitrogen.

It is known to use processes of the methane scrubbing type, described in EP 0 465 366, to separate a synthesis gas into its various constituents. This process is based in particular on the use of a fraction of a fluid rich in methane recovered at the bottom of a CO/CH<sub>4</sub> column as scrubbing fluid, the other fraction of this fluid then being recovered in the form of a methane purge.

The first column carries out a methane scrubbing in order to recover, at the bottom, a fraction rich in CO and in methane and, at the top, a fraction rich in hydrogen.

The second column or stripping column (flash column) is used to discharge the few percent of hydrogen contained in the liquid fraction of the first column.

It is also known, from the patent FR 2 807 505 A1 or FR 2 807 504 A1, to carry out successive coolings of the gas in the methane scrubbing column.

This is because, as the scrubbing is exothermic and more efficient at low temperature, getting closer to the coldest possible temperature makes it possible to improve the efficiency of the methane scrubbing of the first column.

Processes according to the preamble of claim 1 are known from WO2013/178901 and EP 317 851. According to these processes of the prior art, the overhead gas from the stripping column is cooled by means of a dedicated exchanger present in the column or of an auxiliary column associated with the methane scrubbing column.

The present invention makes it possible to improve the performance qualities, by using existing scrubbing column equipment with intermediate gas cooling.

Among the subject matters of the invention, it is desired:

- either to improve the CO recovery efficiency in a synthesis gas separation unit,
- or to optimize the capital cost with the same CO efficiency by a particular arrangement of the stripping column.

The idea of the invention is to cool and to at least partially condense a gas withdrawn in an upper part of the stripping column in an exchanger where at least one intermediate gas of the methane scrubbing column is cooled and to return at least a part of the at least partially condensed gas therefrom to the upper part of the stripping column. The stripping column comprises an upper part and a lower part, below the upper part.

On cooling, this gas withdrawn from the upper part condenses a significant portion of CO and methane. The liquid fraction will fall back as stripping column top reflux and will thereby increase the yield of CO and methane. This makes it possible to partially replace the minaret of EP 0 317 851 A2 and to recover yield for a marginal cost. (see below)

This also makes it possible to render the operation easier. In general, when the stripping column is poorly adjusted, a not insignificant amount of CO leaves at the column top. This cooling thus makes it possible to facilitate the operation of the unit and to be able to compensate for certain losses in CO yield by slightly increasing the flow rate of the cycle compressor.

Different fluids can be used, depending on the columns present, to condense the overhead gas from the stripping column.

Subsequently, in the case where this invention is combined with a stripping column minaret as described in EP 0 317 851-A2, the overhead gas rising in the minaret will enter the scrubbing section at a lower temperature. The methane scrubbing of the minaret will thus be all the more effective.

The CO yield can be increased by approximately 0.5% to 1% compared to the case with the minaret.

This overhead gas from the stripping column can, for example, be cooled countercurrentwise with another fluid from the cold box, such as, for example, liquid CO.

It is advantageous to note that, in the context of methane scrubbing, according to the device described in FR 2 807 505-A1, a liquid CO capacity is installed at the methane scrubbing column top in order to operate at the lowest possible temperature. It would thus suffice to add the gas originating from the stripping column to an exchanger serving to heat the liquid CO originating from the capacity in order to increase the CO recovery yield. This overhead gas from the stripping column represents only a fraction of the synthesis gas flow rate (2-3%), while the gas treated in normal time represents approximately the entire hydrogen flow rate, i.e. 70% of the flow rate. The addition of this stripping column overhead fluid to the exchanger is thus marginal in terms of capital cost and makes it possible to improve the yield.

According to a subject matter of the invention, provision is made for a process for the separation of a synthesis gas comprising hydrogen, carbon monoxide and methane, and possibly nitrogen, by cryogenic distillation, in which:

- i) the synthesis gas is purified and cooled down to a cryogenic temperature,
- ii) the cooled synthesis gas is separated by a first means in order to produce a liquid depleted in hydrogen; the separation carried out by the first means consists of a stage of scrubbing in a scrubbing column with at least a part of the liquid enriched in methane withdrawn from a column for the separation of carbon monoxide and methane having an overhead condenser, the condenser being cooled by a carbon monoxide cycle, and
- iii) the liquid depleted in hydrogen is introduced into the upper part of a stripping column which also comprises a lower part,
- iv) a gas enriched in hydrogen is withdrawn at the top of the stripping column,
- v) a liquid is withdrawn at the bottom of the stripping column and sent to the separation column, a gas enriched in carbon monoxide and depleted in methane is withdrawn at the top of the separation column, a liquid depleted in carbon monoxide and enriched in methane is withdrawn at the bottom of the separation column and the gas enriched in carbon monoxide is heated by heat exchange with the synthesis gas from stage i) in order to form a product,

vi) a gas withdrawn in the upper part of the stripping column is at least partially condensed and returned at least in part to the upper part of the stripping column, characterized in that the gas withdrawn in the upper part of the stripping column is at least partially condensed in a heat exchanger which also serves to cool at least one gas withdrawn from the scrubbing column, the heat exchanger also serving to heat a refrigerant.

According to other optional aspects:

- the gas withdrawn in the upper part of the stripping column condenses against at least a part of the carbon monoxide cycle liquid,
- the synthesis gas comprises nitrogen and the liquid withdrawn from the stripping column or a fluid derived from this liquid is separated in a denitrogenation column, the liquid of which serves to at least partially condense the overhead gas from the stripping column,
- the gas withdrawn in the upper part of the stripping column is at least partially condensed by heat exchange with a liquid enriched in carbon monoxide withdrawn from the separation column, which heats up and optionally vaporizes, at least partially,
- the liquid enriched in carbon monoxide is withdrawn from a distillation section of the separation column or from a capacity forming the top of the separation column,
- the gas withdrawn from the upper part of the stripping column is an overhead gas from the stripping column withdrawn at a level above any heat and mass transfer means of the stripping column,
- the gas withdrawn from the upper part of the stripping column is withdrawn at least one theoretical plate below the top of the stripping column, a part of the liquid enriched in methane withdrawn from the separation column being sent to a level of the stripping column above the level for withdrawal of the gas,
- the separation carried out by the first means does not comprise a stage of scrubbing with a liquid enriched in methane,
- the process is kept cold by a cycle using the gas enriched in carbon monoxide originating from the separation column,

- the liquid depleted in hydrogen contains between 1 mol% and 3 mol% of hydrogen,
- the refrigerant is enriched in carbon monoxide,
- the refrigerant is a liquid enriched in carbon monoxide, optionally originating from the separation column, which vaporizes in the second heat exchanger,
- the second heat exchanger is heated solely by means of the refrigerant.

According to another subject matter of the invention, provision is made for an apparatus for the separation of a synthesis gas comprising hydrogen, carbon monoxide, methane and optionally nitrogen by cryogenic distillation comprising a heat exchanger, a first separation means which is a methane scrubbing column, a stripping column and optionally a column for the separation of carbon monoxide and methane, means for purifying the synthesis gas, means for sending the purified gas to be cooled in the heat exchanger to a cryogenic temperature, means for sending the cooled synthesis gas to the first means for producing a liquid depleted in hydrogen, means for introducing the liquid depleted in hydrogen into the upper part of the stripping column which also comprises a lower part, means for withdrawing a gas enriched in hydrogen at the top of the stripping column, means for withdrawing a liquid at the bottom of the stripping column, a second heat exchanger, means for sending there a gas withdrawn in the upper part of the stripping column and means for sending at least a part of the gas at least partially condensed in the second heat exchanger to the upper part of the stripping column, means for sending the stripping column bottom liquid to the column for the separation of carbon monoxide and methane, means for withdrawing a gas enriched in carbon monoxide and depleted in methane at the top of the separation column, means for withdrawing a liquid depleted in carbon monoxide and enriched in methane at the bottom of the separation column and means for sending the gas enriched in carbon monoxide to heat up in the heat exchanger by heat exchange with the synthesis gas in order to form a product, characterized in that it comprises means for sending at least one gas withdrawn from the scrubbing column to be cooled in

the second heat exchanger and means for sending at least one refrigerant to heat up in the second heat exchanger.

The apparatus can also comprise:

- means for withdrawing the gas in the upper part of the stripping column and for sending it to condense against at least a part of the carbon monoxide cycle liquid,
- if the synthesis gas comprises nitrogen, a denitrogenation column for separating the liquid withdrawn from the stripping column or a fluid derived from this liquid,
- means for sending the liquid withdrawn from the stripping column to serve to at least partially condense the overhead gas from the stripping column,
- means for making possible a heat exchange between the gas withdrawn in the upper part of the stripping column and a liquid enriched in carbon monoxide withdrawn from the separation column, which heats up and optionally vaporizes, at least partially,
- means for withdrawing the liquid enriched in carbon monoxide is from a distillation section of the separation column or from a capacity forming the top of the separation column,
- means for withdrawing the gas withdrawn from the upper part of the stripping column as overhead gas from the stripping column withdrawn at a level above any heat and mass transfer means of the stripping column,
- means for withdrawing the gas withdrawn from the upper part of the stripping column at least one theoretical plate below the top of the stripping column,
- means for sending a part of the liquid enriched in methane withdrawn from the separation column to a level of the stripping column above the level for withdrawal of the gas,
- means for keeping the process cold comprising a cycle using the gas enriched in carbon monoxide originating from the separation column,
- the second heat exchanger is an indirect heat exchanger.

The invention will be described in more detail with reference to the figures, each of which figuratively represents a process according to the invention.

Figure 1 shows a process using a phase separator 9, a methane scrubbing column 15, a stripping column 25 and a column for the separation of carbon monoxide and methane 45, for example containing structured packings for the columns, and capable of operating at cryogenic temperatures.

The synthesis gas 1 containing carbon monoxide, methane and carbon monoxide is purified of water and/or of carbon dioxide in the purification unit 3 before arriving at the heat exchanger 7, where it cools to a cryogenic temperature and partially condenses.

The two phases are separated in a phase separator 9, in order to form a gas 11 enriched in hydrogen and a liquid depleted in hydrogen 13. The gas 11 is sent to the bottom of the methane scrubbing column 15, which produces a gas 19 enriched in hydrogen which is heated in the exchanger. A part of this gas 19 serves to regenerate the purification unit 3.

At least one intermediate gas 21A, 21B, 21C withdrawn from the column 15 is cooled in a heat exchanger 23 by indirect heat exchange with a fluid of the process, in this instance the liquid 51.

The bottom liquid 17 from the column 15 joins the liquid 13 from the separator 9 and the mixture 91, containing between 1 mol% and 3 mol% of hydrogen, is sent to the top of a stripping column 25. An overhead gas 27 from the stripping column condenses at least partially in the heat exchanger 23. A part 31 at least of the at least partially condensed gas is returned at the top of stripping column 25 in order to provide reflux liquid. The remainder 29 can heat up in the heat exchanger 7 against the synthesis gas 5.

The refrigerant gas 27 which leaves to be cooled in the heat exchanger 23 will undergo an at least partial condensation therein. In the case of partial condensations, liquid and gas are created. It is possible that a part of the liquid created passes through another pipe 31 or else falls back via the pipe 27 from which the refrigerant gas to be cooled originates, to join the column 25. In this second case, the pipe 31 is not necessary.

A liquid 33 taken at the bottom of the stripping column 25 cools in the exchanger 7 and is sent to the separation column 45. Another part of the same liquid 35 vaporizes in a bottom reboiler 37 and is returned at the bottom of the stripping column.

The separation column comprises several sections for separation by distillation and optionally a capacity 99. It has a bottom reboiler 73 which serves to heat the bottom liquid 75, the gas formed being returned to the bottom. The bottom liquid 77 enriched in methane is divided into two. A part 83 vaporizes in the exchanger 7 in order to form fuel. The remainder 85 is pressurized by a pump 87 and is sent to the top of the scrubbing column 15.

The overhead gas from the column 43 enriched in carbon monoxide is sent to a product compressor 57, which produces a gas enriched in carbon monoxide 57. A part of the gas enriched in carbon monoxide 61 is cooled and is divided into two. A part 65 is expanded in a turbine 67 in order to provide cold. The expanded gas 89 is returned to the inlet of the compressor 57. The remainder of the gas 69 continues to cool in the exchanger 7 and serves to heat the reboilers 73 and 37 (flows 93 and 73). The gas which has served for the reboiling is thus partially condensed and feeds, as flow 97, the capacity 99 at the top of the separation column 45. The gas 41 from the capacity 99 feeds the compressor 57. The liquid 47 from the capacity 99 is sent to a phase separator 49, the liquid 51 from the separator serves as refrigerant in the heat exchanger 23 in order to cool the intermediate gases 21A, 21B, 21C as well as the overhead gas 27 from the stripping column. The liquid 51 is thus vaporized and returned to the phase separator 49, the gas 53 from which feeds the compressor 57.

A liquid withdrawn from the separation section of the separation column can replace the liquid 47 or another liquid of the process.

According to an alternative form of the process, illustrated in figure 2, the stripping column comprising a methane scrubbing section, a part of the liquid 85 pressurized by the pump 87 being sent to the top of the stripping column 25 and another part being sent, as for figure 1, to the top of the scrubbing column 15.

In this case, the gas 27 withdrawn from the stripping column 25 is taken at least one theoretical plateau below the top of the column.

The gas at least partially condensed in the exchanger 23 returns to the stripping column next to the withdrawal point and the gas rising in the upper part of the stripping column (scrubbing section 25A) becomes more enriched in

hydrogen, making it possible to reduce the number of theoretical plates required.

As shown by figure 3, the invention also applies to the case where the process does not use a methane scrubbing column. In this instance, the first separation is carried out simply by partial condensation in the separator 9. The gas 11 is heated and the liquid depleted in hydrogen 13 is sent to the stripping column 25. The latter may or may not comprise a methane scrubbing section, as for figure 2, according to requirements.

In this instance, the methane scrubbing section 25A is present and thus the gas 27 withdrawn from the stripping column is taken at an intermediate level, as for figure 2.

Thus, all the pressurized methane is sent to the top of the stripping column 25.

In the absence of a scrubbing column 15, the heat exchanger 23 is simplified and makes possible a heat exchange between two fluids alone, the gas to be cooled 27 and the liquid to be heated 51.

If the section 25A is absent, the gas 27 is taken at the top of the column 25.

### Claims

1. A process for the separation of a synthesis gas comprising hydrogen, carbon monoxide and methane, and possibly nitrogen, by cryogenic distillation, in which:

i) the synthesis gas (1, 5) is purified and cooled down to a cryogenic temperature,

ii) the cooled synthesis gas is separated by a first means (9, 15) in order to produce a liquid depleted in hydrogen (91), the separation carried out by the first means consists of a stage of scrubbing in a scrubbing column (15) with at least a part of the liquid enriched in methane withdrawn from a column for the separation of carbon monoxide and methane having an overhead condenser, the condenser being cooled by a carbon monoxide cycle, and

iii) the liquid depleted in hydrogen is introduced into the upper part of a stripping column (25) which also comprises a lower part,

iv) a gas enriched in hydrogen (27, 29) is withdrawn at the top of the stripping column,

v) a liquid (33) is withdrawn at the bottom of the stripping column and sent to the separation column (45), a gas (43) enriched in carbon monoxide and depleted in methane is withdrawn at the top of the separation column, a liquid (77) depleted in carbon monoxide and enriched in methane is withdrawn at the bottom of the separation column and the gas enriched in carbon monoxide is heated by heat exchange with the synthesis gas from stage i) in order to form a product (29),

vi) a gas (27) withdrawn in the upper part of the stripping column is at least partially condensed and returned at least in part to the upper part of the stripping column, characterized in that the gas withdrawn in the upper part of the stripping column is at least partially condensed in a heat exchanger (23) which also serves to cool at least one gas (210, 211) withdrawn from the scrubbing column, the heat exchanger also serving to heat a refrigerant.

2. The process as claimed in claim 1, in which the gas (27) withdrawn in the upper part of the stripping column condenses against at least a part (51) of the carbon monoxide cycle liquid.

3. The process as claimed in either of the preceding claims, in which the synthesis gas (1, 3) comprises nitrogen and the liquid withdrawn from the stripping column (25) or a fluid derived from this liquid is separated in a denitrogenation column (55), the liquid of which serves to at least partially condense the overhead gas from the stripping column.

4. The process as claimed in one of the preceding claims, in which the gas (27) withdrawn in the upper part of the stripping column is at least partially condensed by heat exchange with a liquid enriched in carbon monoxide withdrawn from the separation column (45), which heats up and optionally vaporizes, at least partially.

5. The process as claimed in claim 4, in which the liquid (47) enriched in carbon monoxide is withdrawn from a distillation section of the separation column (45) or from a capacity forming the top of the separation column.

6. The process as claimed in one of the preceding claims, in which the gas withdrawn from the upper part of the stripping column (27) is an overhead gas from the stripping column withdrawn at a level above any heat and mass transfer means of the stripping column.

7. The process as claimed in one of claims 1 to 6, in which the gas withdrawn from the upper part of the stripping column is withdrawn at least one theoretical plate below the top of the stripping column, a part of the liquid enriched in methane withdrawn from the separation column being sent to a level of the stripping column above the level for withdrawal of the gas.

8. The process as claimed in one of claims 1 to 6, in which the separation carried out by the first means does not comprise a stage of washing with a liquid enriched in methane.

9. The process as claimed in one of the preceding claims, which is kept cold by a cycle using the gas enriched in carbon monoxide originating from the separation column (45).

10. The process as claimed in one of the preceding claims, in which the liquid (17) depleted in hydrogen contains between 1 mol% and 3 mol% of hydrogen.

11. An apparatus for the separation of a synthesis gas comprising hydrogen, carbon monoxide, methane and optionally nitrogen by cryogenic distillation comprising a heat exchanger (7), a first separation means (9, 15) which is a methane scrubbing column, a stripping column (25) and optionally a column for the separation (45) of carbon monoxide and methane, means (3) for purifying the synthesis gas, means for sending the purified gas to be cooled in the heat exchanger to a cryogenic temperature, means for sending the cooled synthesis gas to the first means for producing a liquid depleted in hydrogen (17), means for introducing the liquid depleted in hydrogen into the upper part of the stripping column which also comprises a lower part, means for withdrawing a gas enriched in hydrogen (27) at the top of the stripping column, means for withdrawing a liquid (33) at the bottom of the stripping column, a second heat exchanger (23), means for sending there a gas (27) withdrawn in the upper part of the stripping column and means for sending at least a part of the gas at least partially condensed in the second heat exchanger to the upper part of the stripping column, means for sending the stripping column (25) bottom liquid (33) to the column for the separation of carbon monoxide and methane (45), means for withdrawing a gas (43) enriched in carbon monoxide and depleted in methane at the top of the separation column, means for withdrawing a liquid (77) depleted in carbon monoxide and enriched in methane at the bottom of the separation column and means for sending the gas enriched in carbon monoxide

to heat up in the heat exchanger by heat exchange with the synthesis gas in order to form a product, characterized in that it comprises means for sending at least one gas (210, 211) withdrawn from the scrubbing column to be cooled in the second heat exchanger and means for sending at least one refrigerant to heat up in the second heat exchanger.

12. The apparatus as claimed in claim 11, in which the second heat exchanger is an indirect heat exchanger (23).

13. The apparatus as claimed in claim 11 or 12, comprising means for withdrawing the gas in the upper part of the stripping column and for sending it to condense against at least a part of the carbon monoxide cycle liquid (47, 51).

14. The apparatus as claimed in claim 11, 12 or 13, where the refrigerant is a liquid (47, 51) enriched in carbon monoxide and comprising means for withdrawing the liquid enriched in carbon monoxide is from a distillation section of the separation column or from a capacity forming the top of the separation column.

15. The apparatus as claimed in one of claims 11 to 14, in which the means for keeping the process cold comprise a cycle (47, 51, 57, 67) using the gas enriched in carbon monoxide originating from the separation column.