

DESCRIPTION

Process and apparatus for synthesis gas fractionation using
an acidic gas scrub and a cryogenic separating process

The invention relates to a process for fractionation of a crude synthesis gas from which carbon dioxide and sulfur components are separated in an acidic gas scrub to obtain a methane-containing synthesis gas consisting largely of hydrogen and carbon monoxide, from which a carbon monoxide product is subsequently obtained in a cryogenic separating process, wherein in the acidic gas scrub a stripping gas is used at a first pressure level, which stripping gas is made available by a nitrogen source with a second pressure level higher than the first.

The invention relates further to an apparatus for carrying out the process according to the invention.

In the present application, the terms "pressure level" and "temperature level" are used to characterize pressures and temperatures in order to express the idea that parameters for performing the process according to the invention do not have to have an exact value. Instead, they approximate an average value. Corresponding levels lie in disjunct ranges.

Species-related processes and apparatuses are used for example in the production of monoethylene glycol from coal. In this context, with the introduction of oxygen the coal is transformed into a crude synthesis gas by partial oxidation, wherein besides the main components hydrogen and carbon monoxide the crude synthesis gas also contains acidic gases, in particular carbon dioxide and sulfur components as well as water and methane. After cooling and drying, the crude synthesis gas is passed to an acidic gas scrub, in which the acidic gases are separated with the aid of a methanol washing

agent, wherein a methane-containing synthesis gas consisting mainly of hydrogen and carbon monoxide and a washing agent charged with the separated acidic gases are obtained. In order to be able to be reused in the acidic gas separation process, the charged washing agent is regenerated, in which process acidic gases are driven out of by nitrogen used as the stripping gas, usually at a pressure between 1.5 and 3bar(a).

To avoid desublimation, traces of acidic gases and washing agent residues are removed from the synthesis gas in a temperature swing adsorber before it is decomposed to yield a carbon monoxide product and crude hydrogen in a cryogenic condensation process. The crude hydrogen is normally used to regenerate the temperature swing adsorber before it is purified by pressure swing adsorption to yield a hydrogen product, and is then reacted together with the carbon monoxide product to form monoethylene glycol.

The oxygen needed for coal gasification is supplied by a cryogenic air separation unit, which simultaneously also provides nitrogen as the stripping gas for the acidic gas scrub. The nitrogen typically forms in the gas phase in the air separation unit under a pressure between 4 and 6 bar(a), and must therefore be decompressed before it is used in the acidic gas scrub. For the purpose of decompression, the nitrogen is passed across a throttling element, wherein pressure energy is largely lost with no economic benefit.

The object of the present invention is therefore to present processes and apparatuses of the kind described in the introduction, with which it is possible to overcome the disadvantages of the related art.

The object as stated is solved according to the invention in terms of the process in that gas provided from the nitrogen

source is used as a refrigerant in the cryogenic separating process and in this process is decompressed to the first pressure level so that it can subsequently be supplied to the acidic gas scrub as stripping gas.

With the process according to the invention, it is possible to use the nitrogen intended for use as stripping gas to perform the function of refrigerant in the cryogenic unit as well, and satisfy at least a portion of the energy needed for operating the cryogenic separating process from the pressure energy in the gas from the nitrogen source used as stripping gas, which is unused in the related art, and so use it gainfully. The chemical composition of the gas supplied from the nitrogen source is not changed when it is used as a refrigerant, so it does not need to undergo any further treatment to render it usable as stripping gas in the acidic gas scrub.

The pressure level of the carbon monoxide product determines the minimum value of the pressure level under which the gas from the nitrogen source must be supplied to the cryogenic separating process as refrigerant. Particularly if the second pressure level does not reach this minimum, it is suggested to compress the gas supplied from the nitrogen source from the second to a third pressure level, equal to or greater than the minimum value, before it is introduced into the cryogenic separating process.

The quantity of the gas from the nitrogen source which is supplied to the cryogenic separating process and used as refrigerant therein is preferably equal to the quantity of stripping gas needed in the acidic gas scrub, and it is fed in its entirety to the acid gas scrub after it has been decompressed to the first pressure level. However, this does not preclude a greater or lesser quantity of gas from the nitrogen source than the required stripping gas quantity

from being supplied as refrigerant in the cryogenic separating process.

If nitrogen is compressed from the second to a third pressure level before it is used in the cryogenic separating process and the quantity of nitrogen used as refrigerant exceeds the quantity of gas that is forwarded at the first pressure level, it is suggested to decompress the excess gas quantity only down to the second pressure level when it is used as refrigerant in the cryogenic separating process and to return it to the condensation process as refrigerant after compression to the third pressure level again.

On the other hand, if the need for stripping gas in the acidic gas scrub cannot be met fully from the cryogenic separating process, the shortfall may expediently be supplied directly from the nitrogen source, wherein the nitrogen is decompressed from the second to the first pressure level via a throttling element. If the cooling energy that can be generated from the gas from the nitrogen source supplied as refrigerant is not sufficient to conduct the cryogenic separating process, liquid nitrogen may be used additionally as a refrigerant.

The implementation of the process according to the invention is particularly advantageous if the cryogenic separating process is a condensation process.

The condensation process has been a part of the related art and known to the professional community for many years. It is used preferably for fractionation of synthesis gases which are obtained by partial oxidation and accordingly have a high carbon monoxide content and a low methane content. The synthesis gas is partially condensed by cooling to obtain a hydrogen-containing first liquid phase which consists largely of carbon monoxide and methane, from which a second

liquid phase is produced by separating hydrogen in a H_2 stripper column, and from this second liquid phase a carbon monoxide-rich gas phase pure enough to be delivered as a carbon monoxide product and a bottom product consisting largely of methane and carbon monoxide are obtained in a CO/CH_4 separating column. Providing the synthesis gas to be fractionated is cooled to a low enough temperature, in the condensation process it is possible to produce a carbon monoxide product with a yield of more than 85% which has a methane content of less than 100 vppm and can thus be used without any further purification steps to manufacture monoethylene glycol for example.

In order to make the peak refrigeration capacity available that is needed particularly for the cryogenic separating process and to generate a return flow at the head of the CO/CH_4 column, according to the related art a refrigeration cycle driven via a cycle compressor is used, in which either externally supplied nitrogen or internally generated carbon monoxide circulate as the refrigerant.

Both refrigeration cycles are driven via multistage compressors. Whereas in a nitrogen cycle a comparatively inexpensive two-stage compressor can be used, a carbon monoxide compressor entails considerably higher costs. The reason for this is firstly because a carbon monoxide compressor must be configured with at least three compressor stages to avoid thermal decomposition of the carbon monoxide and soot deposits resulting therefrom. Secondly, it must be explosion-proof and must be operated in a specially secured area to prevent escaping carbon monoxide from injuring people or damaging equipment. A compressor for driving a carbon monoxide cycle therefore costs up to 50% more than a compressor designed for a corresponding nitrogen cycle.

The process according to the invention makes it possible to operate the refrigerant cycle of the condensation process with a simpler, less expensive compressor and lower operating costs than in the related art, since the gas from the nitrogen source is already supplied at a higher pressure and therefore needs to undergo less additional compression. Besides the degree of compression of the gas supplied from the nitrogen source, the configuration of the compressor is influenced by the intensity of the third pressure level, which in turn depends primarily on the process control within the condensation process. A condensation process of the kind identified above, in which the CO/CH₄ separating column is heated with nitrogen used as refrigerant and at least a part of the synthesis gas to be fractionated, wherein the second liquid phase is divided into first, second and third partial streams, of which the first is evaporated against the condensing nitrogen that is cooled during the heating of the CO/CH₄ separating column and the second is evaporated against partially condensing synthesis gas, and the vapour phases formed thereby are supplied to the CO/CH₄ separating column as intermediate heating, while the third partial stream is discharged to the CO/CH₄ separating column as an intermediate return flow has been identified as particularly favourable for these purposes.

The carbon monoxide yield from the condensation process depends substantially on the achievable temperature level of the peak refrigeration capacity, which level is determined by the first pressure level. Since nitrogen is used as the refrigerant, a first pressure level between 2 and 3 bar(a) is already sufficient to obtain a yield comparable to that obtained with a considerably more expensive carbon monoxide refrigeration cycle.

In such a condensation process, the nitrogen used as refrigerant is preferably decompressed by less than 13 bar

and particularly preferably by less than 10 bar to reach the first pressure level.

The invention further relates to an apparatus for fractionation of a crude synthesis gas, with an acidic gas scrub for obtaining a methane-containing synthesis gas consisting largely of hydrogen and carbon monoxide by separation of carbon dioxide and sulfur components from the crude synthesis gas and using a stripping gas at a first pressure level, a cryogenic gas fractionation unit in which a carbon monoxide product may be obtained from the synthesis gas, and a nitrogen source from which the stripping gas may be removed at a second pressure level higher than the first.

The object as stated is solved in terms of the apparatus according to the invention in that the cryogenic gas fractionation unit is connected to the acidic gas scrub and the nitrogen source such that gas can be supplied to it from the nitrogen source so that it is able to use the gas as refrigerant and subsequently deliver it to the acidic gas scrub as stripping gas, decompressed to the first pressure level.

In a preferred variant, the apparatus according to the invention comprises a compressor that is connected to the nitrogen source and to the cryogenic gas fractionation unit, via which gas taken from the nitrogen source as refrigerant is compressed to a third pressure level before it is introduced into the cryogenic gas fractionation unit.

The cryogenic gas fractionation unit is particularly preferably designed to carry out a condensation process, for which it comprises at least one heat exchanger for cooling and partial condensation of the synthesis gas, a separator in which a first liquid phase can be separated from the partially condensed synthesis gas, a H₂ stripper column in

which a second liquid phase can be generated from the first liquid phase by separation of hydrogen, and a CO/CH₄ separating column which is connected to a reboiler that is part of a refrigeration cycle and via which heat may be extracted from nitrogen contained in the refrigeration cycle and a part of the synthesis gas that is to be fractionated and supplied to the CO/CH₄ separating column in order to heat it, in order to obtain a carbon monoxide-rich gas phase of such purity that it can be discharged as carbon monoxide product and a bottom product consisting largely of methane and carbon monoxide from the second liquid phase, wherein the second liquid phase may be divided into first, second and third partial streams, of which the first may be evaporated against the condensing nitrogen that is cooled during the heating of the CO/CH₄ separating column and the second may be evaporated against partially condensing synthesis gas, and the vapour phases formed thereby may be supplied to the CO/CH₄ separating column as intermediate heating, while the third partial stream may be discharged to the CO/CH₄ separating column as an intermediate return flow.

In order to supply the particularly preferred cryogenic gas fractionation unit, the gas that is taken from the nitrogen source and used as refrigerant only needs to be comparatively low third pressure level, not more than 13 bar above the first pressure level, so the compression may be effected simply with the use of single-stage compressor if the second pressure level is at least 2 bar higher than the first pressure level.

The nitrogen source is preferably a cryogenic air separation unit which is able to provide nitrogen in the gas phase with a pressure between 4 and 6 bar(a).

The acidic gas scrub is also preferably embodied as a methanol scrubber in which nitrogen at a pressure level

between 1.5 and 3 bar(a) may be used as a stripping gas for washing agent regeneration.

In the following text, the invention will be explained in greater detail with reference to two embodiments thereof represented diagrammatically in Figures 1 and 2.

Figure 1 shows the generation of monoethylene glycol, in which a crude synthesis gas is fractionated in a manner according to the invention.

Figure 2 shows a cryogenic separation device which is operated according to the condensation process, which may advantageously be used when the process according to the invention is carried out.

In Figure 1, a carbon-containing feedstock such as coal or heavy oil is fed via line 1 to reactor R, where it is reacted with oxygen 2 from the cryogenic air separation unit L by partial oxidation to form a crude synthesis gas, which via line 3 passes into the synthesis gas cooler K after soot has been removed. After cooling and drying, the crude synthesis gas 4 is supplied to the acidic gas scrub M, in which carbon dioxide and other acidic gases are separated with the aid of a methanol-washing agent, wherein a methane-containing synthesis gas 5 consisting largely of hydrogen and carbon monoxide, and a washing agent charged with the separated acidic gases are obtained. In order to avoid desublimation in the following process step, remaining traces of acidic gases and washing agent residues are separated from the synthesis gas 5 in temperature swing adsorber A before it is fed via line 6 to the cryogenic separation device T, which is preferably operated as a condensation process. Crude hydrogen 7 obtained in the cryogenic separation device T is first used as a regeneration gas in temperature swing adsorber A and then purified to give a hydrogen product 8 in

the pressure swing adsorber D, which hydrogen product is reacted in the synthesis unit G together with the carbon monoxide product 9, which is also produced in the cryogenic separation device T, to form monoethylene glycol 10. Besides the oxygen 2 needed for the partial oxidation, the cryogenic air separation unit L delivers liquid 11 to meet the refrigeration need of the cryogenic separation device T and gas-phase nitrogen 12 at a pressure level between 4 and 6 bar(a), which is needed as stripping gas in the regeneration of the charged methanol washing agent in the acidic gas scrub M. Before it is used as stripping gas, the gas-phase nitrogen 12 is further compressed to a value between 12 and 16 bar(a) with the aid of the preferably single-stage compressor P and introduced as refrigerant 13 into the refrigeration cycle of the cryogenic separation device T, where it is decompressed with cooling effect to deliver most of the necessary refrigeration capacity. The decompressed nitrogen 14 exits the cryogenic separation device T at the pressure level of the stripping gas and is forwarded to the acidic gas scrub M. If less nitrogen can be used as refrigerant in the cryogenic separation device T than is needed as stripping gas in the acidic gas scrub M, a part 15 of the gas-phase nitrogen 12 is diverted out of the cryogenic air separation unit L upstream of the compressor P and decompressed across the throttling element a before it too is supplied to the acidic gas scrub M as stripping gas.

In the cryogenic separation device T represented in Figure 2, the synthesis gas 6 that has been purified in the temperature swing adsorber A is cooled without condensing against process streams that are to be warmed at a pressure between 30 and 60 bar(a) in a first heat exchanger E1 and then divided into a first 22 and a second partial stream 23, and heat is extracted from the first 22 in the reboiler R to heat the CO/CH₄ separating column T2, giving rise to a further cooled, completely gaseous first partial stream 24, with

which the second partial stream 23, which is routed to the reboiler R in the bypass, is combined to form synthesis gas stream 25. The quantity ratio of the two partial streams 22 and 23 may be varied in order to control the temperature conditions in the CO/CH₄ separating column T2.

In the second heat exchanger E2, the synthesis gas stream 25 is cooled until a two-phase substance mixture 26 is formed by the condensation of components, which mixture is separated in separator B into a hydrogen-containing liquid phase consisting largely of carbon monoxide and methane, and a hydrogen-rich gas phase. The gas phase is extracted from the separator B via line 27, and after warming in the heat exchangers E2 and E1 is used as crude hydrogen 7 to regenerate the temperature swing adsorber A before being forwarded to the pressure swing adsorber D. On the other hand, the liquid phase 29 is supplied to the H₂ separating column T1. For this purpose, it is split into two partial streams, of which the first 30 is decompressed as return flow to the head of the H₂ separating column T1, while the second partial stream 31 is discharged to the middle portion of the H₂ separating column T1 as intermediate heating after decompression and subsequent partial evaporation in the heat exchanger E2.

The H₂ separating column T1, which is operated at a pressure equivalent to between one fifth and one third of the pressure of the synthesis gas 6, is used to remove the hydrogen which is dissolved in the liquid phase 29. It is heated by a circulation heater 32 which is integrated in the heat exchanger E2.

After warming in the heat exchangers E2 and E1, the hydrogen-rich overhead fraction 33 from the H₂ separating column T1 is discharged at the system boundary as flash-gas 28, whereas the largely hydrogen-free bottom fraction 35, consisting of

carbon monoxide and methane, is split into three partial streams 36, 37 and 38 and forwarded for decompression in CO/CH₄ separating column T2, which operates at a pressure between 5 and 10 bar(a). The CO/CH₄ separating column T2 is heated via the reboiler R, in which at least a part of the reboiler stream 39 is evaporated.

The peak refrigeration capacity required for the cryogenic separating process is obtained via a refrigerant circuit which is driven by the compressor P, in which the nitrogen 12 made available in the gas phase by the cryogenic gas fractionation unit L circulates as refrigerant. The nitrogen 13 exits the preferably single-stage compressor P under pressure not more than 13 bar greater than the pressure of the stripping gas needed in the acidic gas scrub M, is then cooled in the heat exchanger E1 and cooled further without condensing in the reboiler R together with the first partial stream 22 of the synthesis gas 6 against the reboiler stream 39 from the CO/CH₄ separating column T2. In the heat exchanger E3, the nitrogen 40 which has been cooled in the reboiler R, is condensed against the partial stream 36, which typically constitutes more than 45% of the quantity of the bottom fraction 35 of the H₂ separating column T1, which consequently evaporates and is transported on as gas stream 42. The second partial stream 37 of the bottom fraction 35 is also evaporated, in heat exchanger E2 against the synthesis gas stream 25 which is to be partly condensed, and as gas stream 43 combined with the gas stream 42 to form gas stream 44, which is then passed into the CO/CH₄ separating column T2 as intermediate heating. The third partial stream 38 of the bottom fraction 35, which only constitutes about 5-10% of the total quantity, is discharged to the CO/CH₄ separating column T2 as intermediate return flow after decompression.

One part 45 of the nitrogen 41 which is condensed in the heat exchanger E3 is decompressed producing refrigeration capacity to the head of the CO/CH₄ separating column T2, where a condenser C is arranged and is cooled by liquid nitrogen to deliver a temperature differential for driving a carbon monoxide return flow 46 inside the column. The second part 47 of the condensed nitrogen 41 and gas-phase nitrogen 48 from the head of the CO/CH₄ separating column T2 are each decompressed to the pressure level of the stripping gas required in the acidic gas scrub, producing refrigeration capacity, and merged with the dual phase nitrogen stream 49, which delivers the peak refrigeration capacity for the cold end of the heat exchanger E2. After evaporation and warming in the heat exchangers E2 and E1, the nitrogen 49 is supplied to the acidic gas scrub M as stripping gas 14.

Below the condenser C, a carbon monoxide fraction 50 having product purity is drawn off from the CO/CH₄ separating column T2 and after warming in the heat exchangers E2 and E1 it is forwarded as carbon monoxide product 9 to the monoethylene glycol synthesis unit G without further compression.

Additional refrigeration capacity is introduced into the separating process via the nitrogen 11 that is drawn in liquid form from the cryogenic air separation unit L and which after evaporation and warming in the heat exchangers E2 and E1 is discharged as a gas phase via line 51 into the atmosphere or a flare system.

A methane-rich, carbon monoxide-containing liquid phase 52, which is also evaporated and warmed in the heat exchangers E2 and E1, collects in the bottom space S of the CO/CH₄ separating column T2 before it can be discharged as fuel gas 53.

CLAIMS

1. Process for fractionation of a crude synthesis gas (4), from which carbon dioxide and sulfur components are separated into an acidic gas scrub (M) to obtain a methane-containing synthesis gas (6) consisting largely of hydrogen and carbon monoxide, from which subsequently in a cryogenic separating process (T) a carbon monoxide product (9) is obtained, wherein in the acidic gas scrub (M) a stripping gas (14) at a first pressure level is employed, which is made available by a nitrogen source (L) having a second pressure level higher than the first pressure level, characterized in that gas (12) provided by the nitrogen source (L) is employed as refrigerant (13) in the cryogenic separating process (T) and is thereby decompressed to the first pressure level in order to subsequently be supplied to the acidic gas scrub as stripping gas (14).
2. Process according to Claim 1, characterized in that gas (12) removed from the nitrogen source (L) as refrigerant is compressed to a third pressure level before it is introduced into the cryogenic separating process (T).
3. Process according to Claim 2, characterized in that nitrogen which is not needed as stripping gas in the acidic gas scrub (M) and is employed as refrigerant (13) in the cryogenic separating process (T) is only decompressed as far as the second pressure level, and following compression to the third pressure level is returned to the condensation process as refrigerant.
4. Process according to any one of Claims 1 to 3, characterized in that the synthesis gas (6) is partially condensed in the cryogenic separating process by cooling to obtain a first, hydrogen-containing liquid phase (29)

consisting largely of carbon monoxide and methane, from which a second liquid phase (35) is generated by separation of hydrogen in a H_2 stripper column (T1), which is separated into a carbon monoxide-rich gas phase (50) of such purity that it can be discharged as carbon monoxide product (9), and a bottom product (52) consisting largely of methane and carbon monoxide in a CO/CH_4 separating column (T2) that is heated by the nitrogen (13) used as refrigerant and at least a part (22) of the synthesis gas (6), wherein the second liquid phase (35) is divided into a first (36), a second (37) and a third partial stream (38), of which the first (36) is evaporated against the condensing nitrogen (40) which is cooled during heating of the CO/CH_4 separating column (T2), and the second (37) is evaporated against partially condensing synthesis gas (25) and the vapour phases (42, 43) formed thereby are supplied to the CO/CH_4 separating column (T2) as intermediate heating, while the third partial stream (38) is discharged to the CO/CH_4 separating column (T2) as intermediate return flow.

5. Process according to Claim 4, characterized in that the nitrogen (13) employed as refrigerant is decompressed by less than 13 bar and preferably by less than 10 bar in the cryogenic separating process (T) to reach the first pressure level.
6. Device for fractionation of a crude synthesis gas (4), with an acidic gas scrub (M) for obtaining a methane-containing synthesis gas (6) consisting largely of hydrogen and carbon monoxide by separating carbon dioxide and sulfur components out of the crude synthesis gas, and with use of a stripping gas (14) at a first pressure level, cryogenic gas fractionation unit (T) in which a carbon monoxide product (9) can be obtained from the synthesis gas (6), and a nitrogen source (L) from

which stripping gas (12) can be drawn at a second pressure level higher than the first, characterized in that the cryogenic gas fractionation unit (T) is connected to the acidic gas scrub (M) and the nitrogen source (L) in such manner that gas (12) can be provided to it from the nitrogen source (L) so that it can be employed as refrigerant and subsequently discharged to the acidic gas scrub as stripping gas (14) after decompression to the first pressure level.

7. Apparatus according to Claim 6, characterized in that it comprises a compressor (P) that is connected to the nitrogen source (L) and the cryogenic gas fractionation unit (T), via which gas (12) taken from the nitrogen source as refrigerant can be compressed to a third pressure level before it is introduced into the cryogenic gas fractionation unit (T).
8. Apparatus according to Claim 7, characterized in that the cryogenic gas fractionation unit (T) comprises at least one heat exchanger (E2) for cooling and partially condensing the synthesis gas (25), a separator (B) in which a first liquid phase (29) can be separated out of the partially condensed synthesis gas (26), a H₂ stripper column (T1), in which a second liquid phase (35) can be produced from the first liquid phase (29) by separating hydrogen, and a CO/CH₄ separating column (T2) which is connected to a reboiler (R), which is part of a refrigeration cycle and via which heat can be extracted from nitrogen (13) that is passed into the refrigeration cycle as well as from a part (22) of the synthesis gas (6) that is to be fractionated and supplied to the CO/CH₄ separating column (T2) to heat it, to obtain a carbon monoxide-rich gas phase (50) sufficiently pure to enable it to be output as carbon monoxide product (9) and a bottom product (52) consisting largely of methane and

carbon monoxide from the second liquid phase (35), wherein the second liquid phase (35) can be divided into a first (36), a second (37) and a third partial stream (38), of which the first (36) can be evaporated against the condensing nitrogen (40) which is cooled during heating of the CO/CH₄ separating column (T2), and the second (37) can be evaporated against partially condensing synthesis gas (25) and the vapour phases (42, 43) formed thereby can be supplied to the CO/CH₄ separating column (T2) as intermediate heating, while the third partial stream (38) can be discharged to the CO/CH₄ separating column (T2) as intermediate return flow.

9. Apparatus according to Claim 8, characterized in that the compressor (P) is of single-stage design.
10. Apparatus according to any one of Claims 6 to 8, characterized in that the nitrogen source (L) is a cryogenic air separation unit.