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(54) Process and installation for supplying gaseous carbon monoxide by cryogenic distillation

(57) In a process for supplying gaseous carbon monoxide by cryogenic distillation, a feed gas (1), containing carbon monoxide as at least one of its principal components and at least one other components chosen from methane, nitrogen and hydrogen, is purified using an adsorption step in one of at least two adsorbent beds (3) to produce a purified feed gas to be sent to the separation unit comprising at least one distillation column (7, 19, 27), the separation unit separates the feed gas to produce gaseous carbon monoxide and the gaseous carbon monoxide is compressed in a product compressor (35) to produce a final product at a product pressure, refrigeration is supplied to the process by a carbon monoxide cooling cycle in which a cycle fluid is compressed in at least the product compressor, cooled and expanded wherein at least part of the carbon monoxide is liquefied to form pressurised liquefied carbon monoxide and part of the pressurised liquefied carbon monoxide (51 A, 53A, 59A), is vaporised at the product pressure to form a pressurised gaseous back-up stream which is then mixed with the final product, vaporisation of the carbon monoxide taking place only when there is an increase in demand for pressurised carbon monoxide.

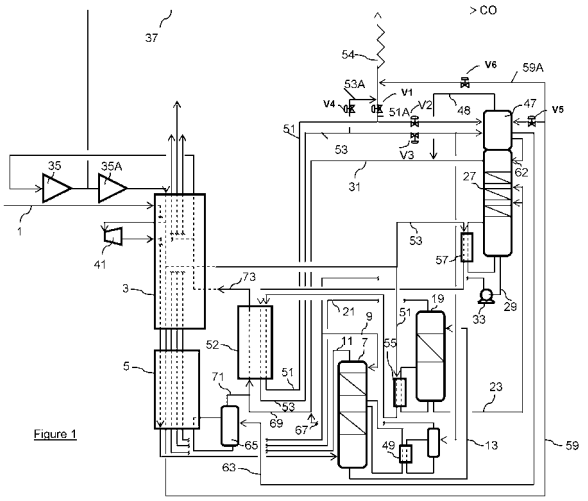

Figure 1

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Description

[0001] This invention concerns processes and installations for providing gaseous carbon monoxide by cryogenic distillation. In particular it concerns the supply of carbon monoxide by vaporisation of liquid carbon monoxide when an industrial installation, such as a separation unit, requires a rapidly increasing amount of gaseous carbon monoxide product.

[0002] It is known from EP-A-1245533 and EP-A-1479989 to produce gaseous carbon monoxide by vaporising liquid carbon monoxide stored at the top of a column for separating carbon monoxide and methane. Since the liquid carbon monoxide is expanded upstream of the column, this means that an additional compression step is required to bring the vapour produced by vaporising the stored liquid back up to the product pressure.

[0003] In order to avoid an additional compression step or dedicated high pressure vessel, the CO liquid is removed before expansion and vaporized at the desired pressure (for example, that of the client's network).

[0004] This allows the change of production rate of the plant to be increased drastically. For example, the amount of gaseous carbon monoxide produced can increase by at least 1 % per minute.

[0005] All percentages mentioned relating to purities are molar percentages and all pressures are absolute pressures.

[0006] According to the present invention, there is provided a process for supplying gaseous carbon monoxide by cryogenic distillation in which:

a) a feed gas, containing carbon monoxide as at least one of its principal components and at least one other components chosen from methane, nitrogen and hydrogen, is purified using an adsorption step in one of at least two adsorbent beds to produce a purified feed gas to be sent to the separation unit comprising at least one distillation column,

b) the separation unit separates the feed gas to produce gaseous carbon monoxide and the gaseous carbon monoxide is compressed in a product compressor to produce a final product at a product pressure

c) refrigeration is supplied to the process by a carbon monoxide cooling cycle in which a cycle fluid is compressed in at least the product compressor, cooled and expanded wherein at least part of the carbon monoxide is liquefied to form pressurised liquefied carbon monoxide and

d) vaporising part of the pressurised liquefied carbon monoxide at the product pressure to form a pressurised gaseous back-up stream which is then mixed with the final product, vaporisation of the carbon monoxide taking place only when there is an increase in demand for pressurised carbon monoxide.

[0007] According to further optional aspects of the invention:

- the separation unit comprises a cryogenic CO/CH_4 distillation column, having a top condenser and/or CO liquid storage capacity and wherein the liquefied carbon monoxide is expanded and sent to the top condenser in normal operation and, if there is an increase in demand for pressurised carbon monoxide, the liquefied carbon monoxide is vaporised without having been sent to the top condenser.
- the liquefied carbon monoxide is vaporised without having been expanded.
- the liquefied carbon monoxide is liquefied by reboiling at least one column of the separation unit.
- the liquefied carbon monoxide in the refrigeration cycle is cooled against the gaseous carbon monoxide, prior to compression of the gaseous carbon monoxide.

[0008] According to another aspect of the invention, there is provided an installation for supplying gaseous carbon monoxide by cryogenic distillation including:

a) a separation unit including at least one distillation column

b) a vaporiser

c) a carbon monoxide product compressor and a product carbon monoxide conduit connected to the outlet of the carbon monoxide product compressor

d) a carbon monoxide refrigeration cycle for cooling the installation, the cycle including conduits for sending refrigeration cycle carbon monoxide to the product compressor, means for liquefying the refrigeration cycle carbon monoxide

e) a conduit for sending liquefied refrigeration cycle carbon monoxide to the vaporiser

f) a back-up conduit for removing vaporised refrigeration cycle carbon monoxide from the vaporiser, the back-up conduit being connected to the product carbon monoxide conduit, there being no compressor between the vaporiser and the point where the back-up conduit connects to the product carbon monoxide conduit

g) a conduit for sending a feed gas containing at least carbon monoxide as a principal component and preferably at least one of nitrogen, methane and hydrogen as other principal components to the separation unit and a conduit for removing gaseous carbon monoxide from the separation unit to the carbon monoxide product compressor and

h) means for controlling the amount of liquefied refrigeration cycle carbon monoxide sent to the vaporiser as a function of the amount of product carbon monoxide required.

[0009] Optional features include:

- the separation unit comprises a cryogenic CO/CH_4

distillation column, having a top condenser and/or CO liquid storage capacity , means for expanding liquefied carbon monoxide and means for sending the expanded liquefied carbon monoxide to the top condenser and/or CO liquid capacity.

- the separation unit comprises a nitrogen wash column
- the separation unit comprises a methane wash column
- there are no means for expanding the liquefied carbon monoxide to be sent to the vaporiser.
- the refrigeration cycle includes means for sending the refrigeration cycle carbon monoxide to a reboiler of at least one column of the separation unit, for example the CO/CH_4 column, and means for sending the refrigeration cycle carbon monoxide liquefied in the reboiler at least to the vaporiser.
- the installation comprises a heat exchanger for cooling the liquefied carbon monoxide by heat exchange with gaseous carbon monoxide and a conduit for sending the warmed carbon monoxide to the product compressor.

[0010] The invention will now be described in greater detail with respect to the figure which is highly simplified but contains the main elements of one installation according to the invention.

[0011] Figure 1 shows an apparatus for separating a mixture containing principally methane, carbon monoxide and hydrogen. The mixture may also contain small amounts of nitrogen, carbon dioxide, humidity, higher hydrocarbons, methanol, etc. This mixture is generally synthesis gas produced by a partial oxidation unit, a steam methane reformer, an auto thermal reformer, gasifier or any combination of these process schemes.

[0012] The mixture 1 is purified in a front end purification unit to remove impurities. Then the mixture is cooled to a cryogenic temperature in heat exchangers 3, 5 and sent to the bottom of a methane wash column 7 operating at a pressure between 10 and 60 bars. A methane wash stream 9 is fed to the top of column 7 and a hydrogen enriched stream 11 is removed from the top of the column. From the bottom of the column is removed a liquid stream 13 enriched in carbon monoxide.

[0013] Stream 13 is further treated before being sent to the stripping column 19 which operates at between 4 and 17 bars, at least one feed stream formed from stream 13 being sent to the top of stripping column 19. Alternatively if a methane stream is fed to the top of stripping column 19, the feed stream is fed thereto at a lower point. The gas 21 from the top of the stripping column is warmed in the exchangers 5,3 and is used as fuel or burnt. The liquid stream 23 from the bottom of the stripping column 19 is divided in two and may be further treated before being sent to the column 27. In particular, several feeds (liquid, dual phase, gaseous, in this case two liquid streams) at different levels may be provided to the column 27. Column 27 operates at between 1 and 10 bars, often around 2.5 bars. There it is separated to form a methane rich liquid 29 at the bottom of the column and a carbon monoxide rich gas 31 at the top of the column. Part of the methane rich liquid is pumped by pump 33 and sent to the top of the methane wash column 7 and the rest is removed as a purge stream. The two portions of the methane rich liquid may be removed separately from the column. In this example, the methane rich liquid is pumped by pump 33 and sent in part to the top of the methane wash column 7 and the remaining purge stream is warmed in heat exchangers 5, 3.

[0014] The carbon monoxide rich product stream 31 removed from the top of column 27 is warmed in a heat exchanger 52 and then in heat exchanger 3, compressed in a compressor 35 and is removed as a compressed product gas 37.

[0015] Refrigeration for the system is provided by a carbon monoxide cycle of which the compressor 35 forms part. The carbon monoxide is compressed in compressor 35 to a pressure of between 10 and 60 bars. Part of the compressed carbon monoxide 39 is further compressed in compressor 35A, then cooled in exchanger 3 to an intermediate temperature of the exchanger and then expanded in turbine 41. The expanded carbon monoxide gas is warmed in the exchanger 3 and recycled to the compressor 35 at the entry thereof or an intermediate pressure thereof. The unexpanded carbon monoxide 43 is divided into three parts, two of which, namely parts 51, 53, serve to reboil columns 9 and 11. Part 51 is sent to reboiler 55 of column 19 and part 53 is sent to the reboiler 57 of column 27. The cooled parts are then both further cooled in heat exchanger 52 from which they are removed as liquid streams. Stream 53 is entirely sent to top condenser and/or CO liquid storage capacity 47 of column 27 via open expansion valve V3. During normal operation, all of stream 51 is also sent to top condenser and/or CO liquid storage capacity 47 via open expansion valve V2, valve V1 being closed.

[0016] The top condenser and/or CO storage liquid capacity 47 forms an integral part of the column 27 and additionally serves to provide reflux to the top of column 27 and to supply liquid carbon monoxide to cool an intermediate reboiler 49 of the methane wash column 7.

[0017] A further part 59 of the unexpanded carbon monoxide 43 is cooled in exchangers 3, 5 and sent to the top condenser or storage 47 via expansion valve V5. In the case where it is required to increase the amount of carbon monoxide produced very quickly, part 59A of the carbon monoxide is sent via open valve V6, which is not an expansion valve, to vaporiser 54, replacing at least one of streams 51, 53 or in addition to at least one of these streams.

[0018] In addition or alternatively, when the amount of product gaseous carbon monoxide required increases rapidly, as a short term measure, part 51A or all of the liquid 51 may be vaporised in a vaporiser 54 upstream of the top condenser and/or CO liquid capacity 47 by opening valve V1 and at least partially closing valve V2.

Since valve is not an expansion valve, the carbon monoxide stream sent to vaporiser 54 is produced substantially at the outlet pressure of compressor 35A, less the pressure drop in the conduits. The vaporiser 54 may either allow heat exchange with ambient air, water or steam if it is outside the cold box or may be within the cold box and may be constituted by the exchanger 5 or another heat exchanger.

[0019] The vaporised carbon monoxide produced 55 is sent to a point downstream of the compressor 35 to form part of the product gas 37.

[0020] Alternatively or additionally, it is possible to vaporise all or part of stream 53 by opening valve V4, which is not an expansion valve and by at least partially closing valve V3 to allow stream 53A to flow to the vaporiser 54.

[0021] Since the liquid to be vaporised 51, 53 is available at high pressure, ie a pressure higher than that of condenser (or storage) 47, the gas produced, by vaporisation in vaporiser 54, can be directly mixed with the product gas 37.

[0022] Gaseous and liquid carbon monoxide are defined to be respectively a gas and a liquid containing at least 85% carbon monoxide, preferably at least 95% carbon monoxide.

[0023] It will be appreciated that the invention applies to other cryogenic separation processes for mixtures containing carbon monoxide and at least one of hydrogen, nitrogen and methane as principal components, for example processes to separate mixtures of hydrogen, carbon monoxide and methane such as the partial condensation process or processes for separating mixtures containing carbon monoxide and nitrogen only as principal components or processes including a nitrogen wash unit.

Claims

1. A process for supplying gaseous carbon monoxide by cryogenic distillation in which:

   a) a feed gas (1), containing carbon monoxide as at least one of its principal components and at least one other components chosen from methane, nitrogen and hydrogen, is purified using an adsorption step in one of at least two adsorbent beds (3) to produce a purified feed gas to be sent to the separation unit comprising at least one distillation column (7, 19, 27),
   b) the separation unit separates the feed gas to produce gaseous carbon monoxide and the gaseous carbon monoxide is compressed in a product compressor (35) to produce a final product at a product pressure
   c) refrigeration is supplied to the process by a carbon monoxide cooling cycle in which a cycle fluid is compressed in at least the product compressor, cooled and expanded wherein at least part of the carbon monoxide is liquefied to form pressurised liquefied carbon monoxide and
   d) part of the pressurised liquefied carbon monoxide (51A, 53A, 59A), is vaporised at the product pressure to form a pressurised gaseous back-up stream which is then mixed with the final product, vaporisation of the carbon monoxide taking place only when there is an increase in demand for pressurised carbon monoxide.

2. A process according to Claim 1 wherein the separation unit comprises a cryogenic CO/CH_4 distillation column (27), having a top condenser and/or CO liquid storage capacity (47) and wherein the liquefied carbon monoxide is expanded and sent to the top condenser in normal operation and, if there is an increase in demand for pressurised carbon monoxide, the liquefied carbon monoxide is vaporised without having been sent to the top condenser.

3. A process according to Claim 2 wherein the liquefied carbon monoxide is vaporised without having been expanded.

4. A process according to any preceding claim wherein the liquefied carbon monoxide is liquefied by reboiling at least one column (19, 27) of the separation unit.

5. A process according to any preceding claims wherein the liquefied carbon monoxide in the refrigeration cycle is cooled against the gaseous carbon monoxide, prior to compression of the gaseous carbon monoxide.

6. An installation for supplying gaseous carbon monoxide by cryogenic distillation including:

   a) a separation unit including at least one distillation column (7, 19, 27)
   b) a vaporiser (54)
   c) a carbon monoxide product compressor (35) and a product carbon monoxide conduit (37) connected to the outlet of the carbon monoxide product compressor
   d) a carbon monoxide refrigeration cycle (3, 5, 41, 55, 57) for cooling the installation, the cycle including conduits for sending refrigeration cycle carbon monoxide to the product compressor and means (55, 57) for liquefying the refrigeration cycle carbon monoxide
   e) a conduit for sending liquefied refrigeration cycle carbon monoxide to the vaporiser
   f) a back-up conduit for removing vaporised refrigeration cycle carbon monoxide from the vaporiser, the back-up conduit being connected to the product carbon monoxide conduit, there being no compressor between the vaporiser and the point where the back-up conduit connects

to the product carbon monoxide conduit
g) a conduit for sending a feed gas containing at least carbon monoxide as a principal component and preferably at least one of nitrogen, methane and hydrogen as other principal components to the separation unit and a conduit for sending gaseous carbon monoxide from the separation unit to the carbon monoxide product compressor and
h) means (V1, V2, V3, V4, V5, V6) for controlling the amount of liquefied refrigeration cycle carbon monoxide sent to the vaporiser as a function of the amount of product carbon monoxide required.

7. An installation according to Claim 6 wherein the separation unit comprises a cryogenic CO/CH_4 distillation column (27), having a top condenser and/or CO liquid storage capacity (47), means for expanding liquefied carbon monoxide and means for sending the expanded liquefied carbon monoxide to the top condenser and/or CO liquid capacity.

8. An installation according to Claim 6 or 7 wherein there are no means for expanding the liquefied carbon monoxide to be sent to the vaporiser (54).

9. An installation according to Claim 6, 7 or 8 wherein the refrigeration cycle includes means for sending the refrigeration cycle carbon monoxide to a reboiler (55, 57) of at least one column (19, 27) of the separation unit and means for sending the refrigeration cycle carbon monoxide liquefied in the reboiler at least to the vaporiser (54).

10. An installation according to any of Claim 6 to 9 comprising a heat exchanger (52) for cooling the liquefied carbon monoxide by heat exchange with gaseous carbon monoxide and a conduit (73) for sending the warmed carbon monoxide to the product compressor.

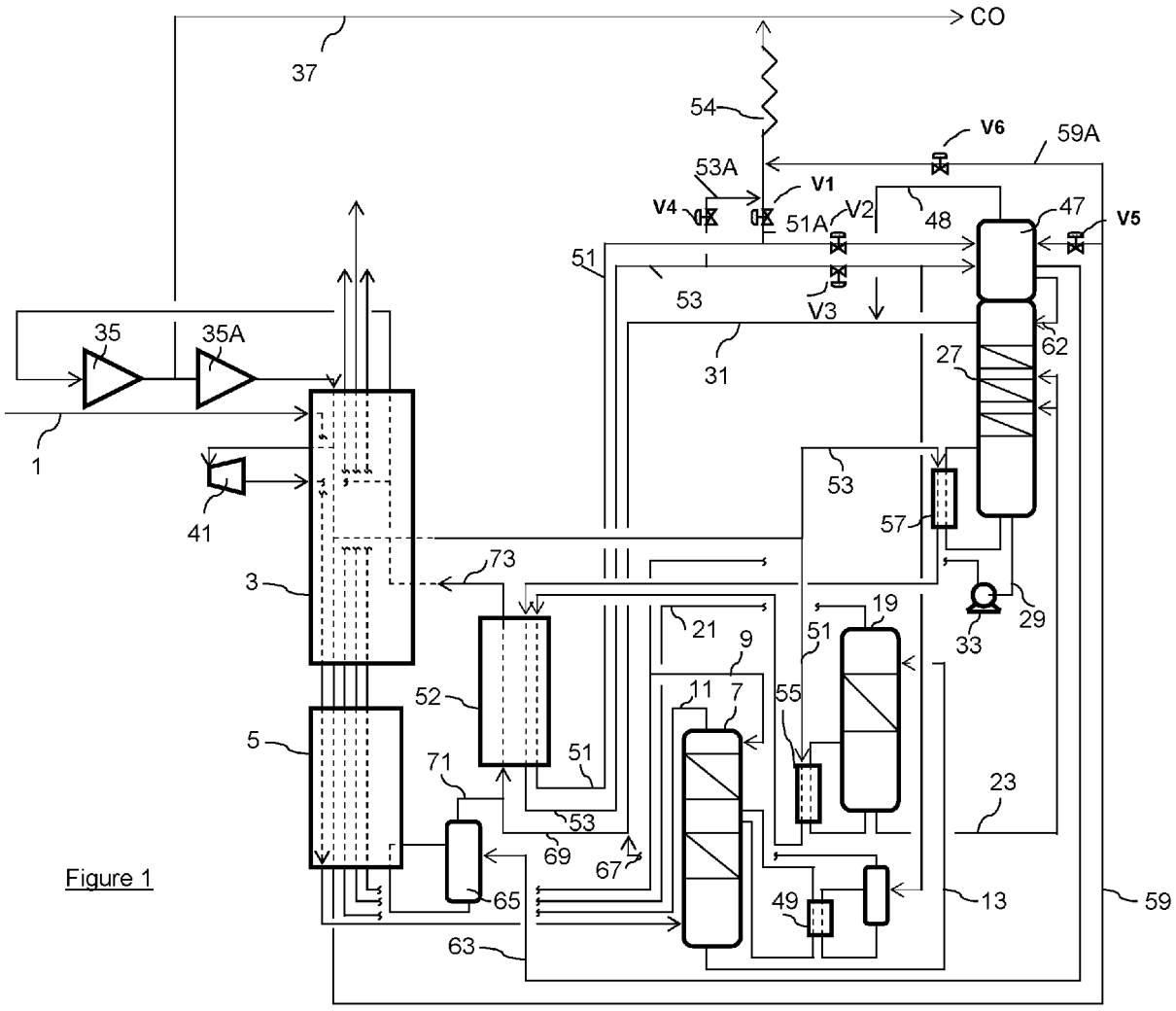
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Figure 1

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EUROPEAN SEARCH REPORT

Application Number
EP 11 30 6060

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F25J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	4 May 2012	Göritz, Dirk

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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