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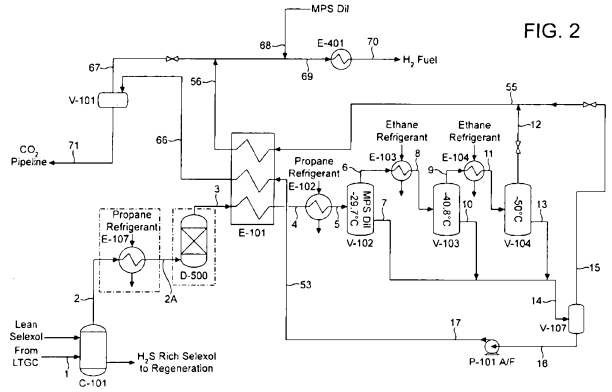
(54) **Title**: SEPARATION OF CARBON DIOXIDE AND HYDROGEN

FIG. 2



(57) **Abstract**: A process is described for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant. In an example described the synthesis gas feed stream (3) comprises 40 to 65 mole % hydrogen and is fed to a single stage or a first stage of a series of separation stages (120, 103, 104) at a pressure in the range of 46 to 90 bar absolute. The single stage or a stage of the series is operated at a temperature in the range of -53 to -48 0C and a pressure in the range of 44 to 90 bar absolute. In some examples, the single stage or the combined stages of the series remove 70 to 80 % of the total moles of carbon dioxide in the synthesis gas feed stream. Liquefied C02 product stream(s) discharged from the stage (s) (7,10,13) of the cryogenic separation plant may be sequestrated and/or used in a chemical process (71).

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SEPARATION OF CARBON DIOXIDE AND HYDROGEN

This invention relates to the partial recovery of carbon dioxide from a synthesis gas stream comprising hydrogen and carbon dioxide thereby generating a carbon dioxide stream that may be used in a chemical process, or may be sequestered or used for enhanced oil recovery before being ultimately sequestered, and a hydrogen stream that may be used as fuel for a power plant thereby generating electricity or as fuel for a burner, furnace or boiler or as a refinery feed stream for upgrading of one or more refinery streams or as a hydrogen feed to a chemical process.

US 2007/0221541 relates to a multi-stage autorefrigeration process where the first two autorefrigeration stages combined remove about 76% of the total moles of acid gases and about the same percentage of moles of CO_2 in the starting syngas. It is said that if the sulfur had been removed from the syngas initially during syngas production, a removal percentage of 76% could quite possibly be, depending on the future of environmental law, adequate for sequestration of CO_2. In such a case, no additional autorefrigeration stages would be needed. However, a disadvantage of the process of US 2007/0221541 is that the liquefied acid gases that are separated in the two autorefrigeration stages are evaporated to provide the cooling of the syngas. Accordingly, it would be necessary to pressurize the acid gas product streams from the stages before they can be sequestered.

It has now been found that at least 70% of the moles of CO_2 can be removed from the starting synthesis gas using a refrigeration process comprising at least one refrigeration stage that employs an external refrigerant by operating the refrigeration stage(s) under optimum conditions of temperature and pressure.

Thus, the present invention provides a process for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant that comprises either a single cryogenic separation stage or at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, the single stage or each stage of the series comprising the steps of (a) condensing carbon dioxide from the synthesis gas by cooling the synthesis gas by non-contact heat exchange with an external refrigerant to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the synthesis gas, with the single separation stage discharging a liquefied carbon dioxide product stream

and a hydrogen enriched synthesis gas stream or, with each of the stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a hydrogen enriched synthesis gas vapour stream, wherein:

(i) the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to the single stage or the first stage of the series at a pressure in the range of 46 to 90 bar, optionally to 76 bar absolute;

(ii) the single stage or stage N of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to 74 bar absolute such that the single stage or the combined stages of the series remove 70 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream; and

(iii) the liquefied CO_2 product stream(s) removed from the stage(s) of the cryogenic separation plant is sequestrated and/or used in a chemical process.

In some aspects of the invention, a higher pressure would be used. For example, in some cases, the pressure of the gas feed itself may already be higher than 74 bar. Alternatively, or in addition, the pressure of the feed may be increased, for example using a series of compressors, or a single compressor, before separation.

A further aspect of the invention provides a process for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant that comprises either a single cryogenic separation stage or at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, the single stage or each stage of the series comprising the steps of (a) condensing carbon dioxide from the synthesis gas by cooling the synthesis gas by non-contact heat exchange with a refrigerant (optionally an external refrigerant) to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the synthesis gas, with the single separation stage discharging a liquefied carbon dioxide product stream and a hydrogen enriched synthesis gas stream or, with each of the stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a hydrogen enriched synthesis gas vapour stream, wherein:

(i) the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to the single stage or the first stage of the series at a pressure in the range of 46 to less than 150 bar absolute;

(ii) the single stage or stage N of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to less than 150 bar absolute; and

(iii) preferably the liquefied CO_2 product stream(s) removed from the stage(s) of the cryogenic separation plant is preferably sequestrated and/or used in a chemical process.

In examples, the pressure may be less than 120 bar, 100 bar, or less than about 80 bar. It will be understood that different % separation of the CO2 will be obtained depending on the pressure and temperature of separation.

A further aspect of the invention provides a process for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant that comprises either a single cryogenic separation stage or at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, the single stage or each stage of the series comprising the steps of (a) condensing carbon dioxide from the synthesis gas by cooling the synthesis gas by non-contact heat exchange with a refrigerant (optionally an external refrigerant) to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the synthesis gas, with the single separation stage discharging a liquefied carbon dioxide product stream and a hydrogen enriched synthesis gas stream or, with stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a hydrogen enriched synthesis gas vapour stream, wherein:

(i) the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to the single stage or the first stage of the series at a pressure in the range of 46 to 76 bar absolute;

(ii) the single stage or first stage of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to 74 bar absolute

In some examples, the single stage or the first stage of the series removes 70 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream. In other examples, about 60% to 90% or more may be removed.

Preferably , the refrigeration process is a multi-stage refrigeration process having at least two refrigeration stages arranged in series that each employ an external refrigerant. In other examples, other coolants or refrigerants might be used, for example as described below. Thus, in a preferred embodiment of the present invention there is provided a process for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant that comprises at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, each stage comprising the steps of (a) condensing carbon dioxide from the synthesis gas by cooling the synthesis gas by non-contact heat exchange with an external refrigerant to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the synthesis gas, with each of the stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a hydrogen enriched synthesis gas vapour stream, wherein:

(i) the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to the first stage of the cryogenic separation plant at a pressure in the range of 46 to 76 bar absolute;

(ii) stage N of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to 74 bar absolute such that the combined stages of the series remove 70 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream; and

(iii) the liquefied CO_2 product streams removed from each stage of the series are sequestrated and/or used in a chemical process.

The term "synthesis gas feed stream" used herein refers to a shifted synthesis gas stream comprising hydrogen and carbon dioxide. The synthesis gas feed stream may also comprise carbon monoxide and hydrogen sulfide.

Where the refrigeration process is a multi-stage refrigeration process, preferably, the liquefied CO_2 product streams that are removed from each stage of the series are combined prior to being sequestrated.

In some examples, 75 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream is separated in the cryogenic separation plant. Thus, the process of the present invention removes a substantial amount of CO_2 from the synthesis gas feed stream.

Typically, the hydrogen enriched synthesis gas stream is fed to the combustor of a gas turbine of a power plant. Accordingly, an advantage of the present invention is that significantly less CO_2 is released to the atmosphere than if the solid fuel or gaseous hydrocarbon feedstock that is used to form the synthesis gas was used directly as fuel for the power plant. A further advantage of the process of the present invention is that the hydrogen enriched synthesis gas stream may be obtained at a pressure that is at or above the minimum fuel gas feed pressure (inlet pressure) for the combustor(s) of the gas turbine(s) of the power plant thereby eliminating the need for compressors to compress the fuel gas.

The synthesis gas feed stream may be generated from a solid fuel such as petroleum coke or coal in a gasifier or from a gaseous hydrocarbon feedstock in a reformer. The synthesis gas stream from the gasifier or reformer contains high amounts of carbon monoxide. Accordingly, the synthesis gas stream is typically treated in a shift converter unit such that at least a portion, preferably, substantially all of the carbon monoxide contained in the synthesis gas stream is converted to carbon dioxide over a shift catalyst according to the water gas shift reaction (WGSR):

$$CO + H_2O \rightarrow CO_2 + H_2.$$

Where a portion of the carbon monoxide remains in the shifted synthesis gas, the majority of this carbon monoxide will be retained in the hydrogen enriched synthesis gas stream and will be converted into carbon dioxide when the hydrogen enriched synthesis gas stream is used as a fuel.

The shift converter unit may be a single shift reactor containing a shift catalyst. However, it is preferred that the shift converter unit comprises a high temperature shift reactor containing a high temperature shift catalyst and a low temperature shift reactor containing a low temperature shift catalyst. The water gas shift reaction is exothermic and results in a significant temperature rise across the shift converter unit. Accordingly, the shift converter unit may be cooled by continuously removing a portion of the shifted synthesis gas stream and cooling this stream by heat exchange with one or more process streams, for example against boiler feed water or against steam (for the generation of superheated steam).

The synthesis gas feed stream typically comprises primarily hydrogen, carbon dioxide and steam and minor amounts of carbon monoxide and methane. Where the

synthesis gas feed stream is derived from a gasifier, the synthesis gas feed stream will also comprise hydrogen sulfide (H_2S) that is formed by reaction of COS with steam in the shift converter unit. A further advantage of the process of the present invention is that it allows the co-capture of the H_2S in addition to capture of carbon dioxide (CO_2). Thus, H_2S will condense from the synthesis gas in the single stage or each of the stages of the series and will be removed from the single stage or each of the stages of the series in the liquefied carbon dioxide product stream(s). By operating the single stage or the final stage of the series (stage N) at a temperature in the range of -53 to -48°C and a pressure in the range of 55 to 59 bar absolute, the single stage or the combined stages of the series will also remove 80 to 90% of the total moles of hydrogen sulfide from the synthesis gas feed stream.

The synthesis gas feed stream is cooled upstream of the cryogenic separation plant, for example, to a temperature in the range of 20 to 50°C, for example, about 40°C to condense out a condensate (predominantly comprised of water). The condensate is then separated from the cooled shifted synthesis gas stream, for example, in a condensate drum. Typically, the condensate is cooled against boiler feed water and/or utility cooling water.

After removal of any condensate, the synthesis gas feed stream is dried prior to being passed to the CO_2 condensation plant, as any moisture in the synthesis gas feed stream will freeze and potentially cause blockages in the plant. The synthesis gas feed stream may be dried by being passed through a molecular sieve bed or an absorption tower that employs triethylene glycol to selectively absorb the water, preferably a molecular sieve bed. Preferably, the dried synthesis gas feed stream has a water content of less than 1 ppm (on a molar basis).

Preferably, the dried synthesis gas feed stream is then passed to a pre-cooling heat exchanger of the CO_2 condensation plant where the synthesis gas feed stream is pre-cooled against a cold stream (for example, a cold process stream such as a liquid CO_2 product stream or a cold H_2 enriched synthesis gas vapour stream). Preferably, the pre-cooling heat exchanger is a multichannel heat exchanger, for example, a plate fin heat exchanger or a printed circuit heat exchanger, with the dried synthesis gas feed stream being passed through at least one channel of the multichannel heat exchanger and a plurality of cold process streams being passed through further channels of the multichannel heat exchanger such that the dried synthesis gas stream is pre-cooled against the cold process streams. Alternatively, the dried synthesis gas feed stream may be pre-cooled against a plurality of

cold process streams using at least two, preferably, 2 to 8, for example, 4 shell and tube heat exchangers. These shell and tube heat exchangers may be arranged in series and/or in parallel. Where the shell and tube heat exchangers are arranged in parallel, the synthesis gas feed stream is divided to form a plurality of sub-streams that are fed to the heat exchangers and the cooled sub-streams that exit the heat exchangers are subsequently recombined. It is also envisaged that the dried synthesis gas stream may be pre-cooled using a combination of a multichannel heat exchanger and one or more shell and tube heat exchangers.

As discussed below, the hydrogen enriched synthesis gas vapour stream may be subjected to isentropic expansion in a turboexpander (resulting in cooling of the hydrogen enriched synthesis gas vapour stream) after being used to pre-cool the dried synthesis gas feed stream. Cooling of the expanded hydrogen enriched synthesis gas vapour stream allows the dried synthesis gas feed stream to be pre-cooled to a temperature in the range of -15 to -35°C, for example, about -23°C. Where the hydrogen enriched synthesis gas vapour stream is not subjected to isentropic expansion before being used to pre-cool the dried synthesis gas stream, the synthesis gas feed stream may typically only be cooled to a temperature in the range of 0 to -15°C, for example, about -10°C. Depending upon the composition of the synthesis gas feed stream and the amount of pre-cooling, the pre-cooled stream may remain in a vapour state or may be cooled to below its dew point thereby becoming two phase.

The synthesis gas feed stream is then passed through the cryogenic separation stage(s) of the cryogenic separation plant. The single cryogenic separation stage or each cryogenic separation stage of the series comprises a heat exchanger that employs an external refrigerant and a gas-liquid separation vessel. Preferably, the cryogenic separation plant comprises 1 to 5, more preferably, 2 to 4, for example, 3 cryogenic separation stages arranged in series.

The term "refrigerant" used herein preferably includes any appropriate coolant or refrigerant. Furthermore, the term "coolant" preferably includes any appropriate coolant or refrigerant.

Preferably the term "internal coolant streams" includes product streams produced in the process. For example the internal coolant streams include CO_2-rich streams and H_2-rich streams formed in the separation step(s). Preferably, where appropriate, the term

"internal coolant streams" includes any appropriate coolant or refrigerant stream.

Preferably the terms "external refrigerant" or "external coolant" include a refrigerant or coolant that is provided in an external refrigeration circuit. Accordingly, liquid CO_2 that is formed in the process of the present invention will not generally be regarded as an external refrigerant. Suitable external refrigerants that may be used as refrigerant in the heat exchanger(s) include propane, ethane, propene, ethylene, ammonia, hydrochlorofluorocarbons (HCFCs) and mixed refrigerants. Typical mixed refrigerants comprise at least two refrigerants selected from the group consisting of butanes, propanes, ethane, and ethylene. These refrigerants may be cooled to the desired refrigeration temperature in external refrigerant circuits using any method known to the person skilled in the art including methods known in the production of liquefied natural gas (LNG) or natural gas liquids (NGLs).

The operating temperature of each cryogenic separation stage will depend on the number of cryogenic separation stages and the desired carbon dioxide capture level. There is a limit on the lowest temperature in the final cryogenic separation stage, as the temperature must be maintained above a value where solid CO_2 will form. This typically occurs at a temperature of less than -55°C at pressures of less than 300 barg (the triple point for pure CO_2 is at 5.18 bar and at a temperature of -56.4°C) although the presence of H_2S may depress this freezing point.

There is preferably minimal pressure drop across the stages of the cryogenic separation plant. Typically, the pressure drop across the single stage or the series of stages of the cryogenic separation plant is in the range of 2 to 10 bar, preferably, 2 to 5 bar, in particular, 2 to 3 bar. Preferably, the pressure drop across the single stage or across each stage of the series is about 1 bar. Thus, where the plant comprises at least two stages arranged in series, it may be operated with the stages at substantially the same pressure. Higher pressure drops across the cryogenic separation stage(s) may be tolerated (for example, pressure drops in the range of 10 to 30 bar, preferably 10 to 20 bar) provided that the single separation stage or final cryogenic separation stage of the series is operated at a pressure in the range of 45 to 59 bar absolute, preferably, 56 to 58 bar absolute, for example, 57 bar absolute. An advantage of operating the single or final cryogenic separation stage of the series at a pressure in the range of 55 to 59 bar absolute is that the H_2 enriched synthesis gas stream that is discharged from the separator vessel of the single

separation stage or from the separator vessel of the final stage (stage N) of the series is at or above the minimum feed gas pressure (minimum inlet pressure) for the combustor(s) of the gas turbine(s) of the power plant (see below).

The process of some examples of some aspects of the present invention will now be described with respect to a CO_2 condensation plant that comprises three cryogenic separation stages arranged in series. The synthesis gas feed stream is pre-cooled against one or more cold process streams (for example, a hydrogen enriched synthesis gas vapour stream and/or a liquefied CO_2 stream) before being passed through the heat exchanger of the first cryogenic separation stage where the synthesis gas is cooled to a temperature in the range of -32 to -28°C against an external refrigerant thereby forming a two phase stream comprising a liquid phase (comprising liquid CO_2) and a vapour phase comprising H_2 and CO_2 (hydrogen enriched synthesis gas). The two phase stream is then passed to the gas-liquid separator vessel of the first cryogenic separation stage where the liquid phase is separated from the vapour phase. A hydrogen enriched synthesis gas vapour stream and a liquid CO_2 stream are withdrawn from the separator vessel, preferably, from at or near the top and bottom respectively of the separator vessel. The H_2 enriched synthesis gas vapour stream is then used as feed to the second cryogenic separation stage where it is passed through a further heat exchanger and is cooled to a temperature in the range of -43 to -39°C against a further external refrigerant. The resulting two phase stream is passed to the gas-liquid separator vessel of the second cryogenic separation stage for separation of the phases. A vapour stream that is further enriched in H_2 and a liquid CO_2 stream are withdrawn from the separator vessel, preferably, from at or near the top and bottom respectively of the separator vessel. The hydrogen enriched synthesis gas vapour stream discharged from the second cryogenic separation stage is then used as feed to the third cryogenic separation stage where it is passed through a further heat exchanger and is cooled to a temperature in the range of -53 to -48°C against a further external refrigerant. The resulting two phase stream is passed to the gas-liquid separator vessel of the third cryogenic separation stage for separation of the phases. A vapour stream that is further enriched in H_2 and a liquid CO_2 stream are withdrawn from the separator vessel, preferably, from at or near the top and bottom respectively of the separator vessel. Preferably, the synthesis gas feed stream is fed to the first cryogenic separation stage at as high a pressure as possible, which will be dependent upon the source of the gas. Typically,

the synthesis gas feed stream is fed to the first cryogenic separation stage at a pressure of at least 50 bar absolute, preferably, 55 to 75 bar absolute, for example, 60 to 70 bar absolute. If desired, the feed to the first cryogenic separation stage may be compressed to higher pressure. Typically, the pressure drop across the three cryogenic separation stages is minimized such that the third cryogenic separation stage is operated at a pressure that is less than 5 bar below the pressure of the first cryogenic separation stage. For example, where the synthesis gas feed stream is fed to the first cryogenic separation stage at a pressure of 60 bar absolute, the third cryogenic separation stage is typically operating at a pressure in the range of 55 to 58 bar absolute.

Typically, the hydrogen enriched synthesis vapour stream (non-condensable stream) discharged from the final cryogenic separation stage (Stage N) of the cryogenic separation plant comprises at least 70 mole % hydrogen, preferably, at least 80 mole % hydrogen, the remainder being mostly carbon dioxide. Typically, the amount of CO_2 contained in the H_2 enriched synthesis gas vapour stream that is discharged from the final cryogenic separation stage (Stage N) of the cryogenic separation plant is less than 30 mole % CO_2, preferably, less than 25 mole % CO_2. This hydrogen enriched synthesis gas vapour stream may also comprise trace amounts of carbon monoxide (CO) and methane, for example, less than 500 ppm on a molar basis (although higher amounts of CO may be tolerated, for example 2-3 mole% CO). The H_2 enriched synthesis gas vapour stream from the final cryogenic separation stage of the CO_2 condensation plant (Stage N) may be used as a fuel stream for the combustor of a gas turbine that drives an electric generator thereby producing electricity.

Typically, the fuel gas feed pressure (inlet pressure) for the combustor of the gas turbine(s) is in the range of 25 to 45 barg, preferably, 28 to 40 barg, in particular, 30 to 35 barg. Typically, the combustor of the gas turbine(s) is operated at a pressure of 15 to 20 bar absolute. Accordingly, the H_2 enriched synthesis gas vapour stream may be obtained above the minimum fuel gas feed pressure for the combustor(s) of the gas turbine(s) so that there is no requirement for a gas compressor to compress the hydrogen enriched synthesis gas stream (fuel gas stream) to the inlet pressure for the combustor(s) of the gas turbine(s). Typically, the H_2 enriched synthesis gas vapour stream may be expanded in at least one turboexpander arranged in series down to the inlet pressure of the combustor(s) of the gas turbine(s). The isentropic expansion of the hydrogen enriched vapour stream in the

turboexpander(s) produces work that may be used to drive at least one turbine or an electric motor thereby generating electricity for export or for use within the process (for example, for operating the CO_2 pumps and/or a compressor of an external refrigeration circuit). Generally, the turboexpanders are mounted on a common shaft. Typically, the turboexpanders are operated with substantially the same pressure ratio across each turboexpander, for example, a pressure ratio in the range of 0.88 to 0.66. The H_2 enriched synthesis gas vapour stream is cooled by isentropic expansion in the turboexpander(s) thereby allowing additional pre-cooling of the synthesis gas feed stream. Typically, the H_2 enriched synthesis gas vapour stream that exits the separator of the single cryogenic separation stage or that exits stage N of the series of cryogenic separation stages is passed through a channel of the multichannel heat exchanger in heat exchanger relationship with the synthesis gas feed stream and is then cooled by expansion to lower pressure in a first turboexpander before being fed to a further channel in the multichannel heat exchanger. The hydrogen enriched vapour stream may then be cooled by expansion to a lower pressure in a second turboexpander before being fed to a further channel of the multichannel heat exchanger. Where the H_2 enriched synthesis gas vapour stream is to be used as fuel gas for the combustor of a gas turbine, it should not be reduced in pressure to below the desired fuel gas feed pressure (inlet pressure) for the combustor. However, it is also recognised that the hydrogen enriched synthesis gas vapour stream may be expanded to pressures below the inlet pressure of the combustor of a gas turbine, if the hydrogen enriched synthesis gas vapour stream is to be used for a different purpose, for example, as fuel for a low pressure burner of a fired heater, or as fuel for a reformer or boiler or as a refinery feed stream for upgrading of one or more refinery streams or as a hydrogen feed to a chemical process.

International Patent Application No PCT/GB2009/001810 describes processes in which H2-enriched gas vapour streams are fed to a turboexpansion system in which the hydrogen rich vapour stream is subjected to isentropic expansion in each of a plurality of turboexpanders of the series such that hydrogen rich vapour streams are withdrawn from the turboexpanders of the series at reduced temperature and at successively reduced pressures thereby generating motive power. Additionally, a cooled hydrogen rich vapour stream can be passed in heat exchanger relationship with a (higher temperature) gas feed stream and thus be used as an internal coolant in the system.

In examples described in International Patent Application No. PCT/GB2009/001810, a synthesis feed gas stream is increased in pressure to a pressure in the range of 150 to 400 barg before it is cooled and passed to separator for withdrawing of the hydrogen enriched gas vapour stream.

As discussed herein, in accordance with aspects of the present invention, it has been identified that a turboexpander system can be advantageously be used also where the separation step is carried out at pressures lower than 150 barg.

Accordingly, a further aspect of the invention provides a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed, the cooling including feeding synthesis gas to a heat exchanger system, preferably in heat exchange relationship with an internal coolant stream that is produced subsequently in the process wherein the internal coolant stream is selected from the group consisting of a hydrogen rich vapour stream and a dense carbon dioxide stream,

b) passing the cooled stream formed in step (a) either directly or indirectly to a gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from separator vessel; and

d) feeding a hydrogen-rich stream to an expansion system including at least one expander, preferably a plurality of expanders, and reducing the pressure of the hydrogen-rich gas at the or each expander.

Preferably the method includes using an expanded hydrogen stream as a coolant in the system.

Preferably one or more methods of the present invention of any aspect as appropriate includes the step of feeding a hydrogen rich stream to an expansion system including at least one expander for reducing the pressure of the hydrogen-rich stream. Preferably expansion system includes a plurality of expanders arranged in series. Preferably the expansion system includes one or more expanders able to recover work from the expansion, for example turboexpanders or a series of turboexpanders. In preferred

examples, the hydrogen-rich gas is fed to a turboexpansion system including a plurality of turboexpanders arranged in series, wherein the hydrogen rich vapour stream is subjected to isentropic expansion in each of the turboexpanders of the series such that a hydrogen rich vapour stream is withdrawn from each of turboexpanders at reduced temperature and at successively reduced pressures and wherein isentropic expansion of the hydrogen rich vapour in each of the turboexpanders of the series generates motive power.

Preferably the temperature of the hydrogen-rich stream is reduced by the expansion and the cooled expanded hydrogen stream is subsequently used as an internal coolant in the system. Preferably the cooled stream from each expander is used as an internal coolant, for example prior to being fed to a further expander.

According to a further aspect of the invention there is provided a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed,

b) passing the cooled stream formed in step (a) either directly or indirectly to a gas-liquid separator vessel, optionally the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from separator vessel; and

d) feeding a separated hydrogen rich vapour stream to an expansion system including a plurality of expanders arranged in series, wherein the hydrogen rich vapour stream is subjected to expansion in each of the expanders of the series such that an expanded hydrogen rich vapour stream is withdrawn from each of the expanders at reduced temperature and at successively reduced pressures; and

e) using at least one expanded hydrogen-rich vapour stream as a coolant.

In some examples, the expansion system might include only one expander wherein the hydrogen rich vapour stream is subjected to expansion in the expander of the system such that an expanded hydrogen rich vapour stream is withdrawn from the expander at reduced temperature and at pressure and used as a coolant. However, in many examples it will be preferred for at least two expanders to be used so that improved temperature and/or

pressure profiles of the process can be sought. As discussed further below, by using more than one expander, in some examples a plurality of relatively cold expanded hydrogen streams can be used as internal coolant streams in the system.

The expanded hydrogen-rich vapour stream may be used to cool one or more streams selected from a hydrogen-rich gas stream, a carbon dioxide stream and a synthesis gas stream.

In preferred examples, a plurality of expanded hydrogen rich vapour streams are used as coolant streams in the process. In some examples, all of the expanded hydrogen rich streams are used as internal coolants.

Preferably the expanders effect isentropic expansion of the hydrogen rich vapour in each of the expanders of the series and generate motive power.

The motive power may for example be further used in the process, leading to efficiencies. For example, the expander may include an expansion turbine preferably connected to a compressor (if used) in the system. Alternatively or in addition, other expanders may be used in some examples. For example, the stream may be expanded across a valve to reduce the pressure.

The method may further include increasing the pressure of the separated carbon dioxide stream.

In some examples, the further utilisation of the carbon dioxide stream, for example for effecting storage, may require a higher pressure than the pressure of the stream withdrawn from the separator. Apparatus, for example a pump, may be provided downstream of the separator to increase the pressure, for example to above 120 bar, or to 150 bar or above.

The method may further include passing the separated hydrogen rich stream directly or indirectly to a further gas-liquid separator vessel and withdrawing a second separated hydrogen rich vapour stream from the separator vessel and a second liquid CO_2 stream from separator vessel.

A further aspect of the invention provides a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed,

b) passing the cooled stream formed in step (a) either directly or indirectly to a first gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from separator vessel;

d) passing the hydrogen rich vapour stream formed in step (c) either directly or indirectly to a second gas-liquid separator vessel, and withdrawing a second hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from separator vessel; and

e) feeding a separated hydrogen rich vapour stream to an expansion system including at least one expander, wherein the hydrogen rich vapour stream is subjected to expansion in the expander of the system such that an expanded hydrogen rich vapour stream is withdrawn from the expander at reduced temperature and at pressure; and

f) using an expanded hydrogen-rich vapour stream as a coolant.

The method may further include cooling the separated hydrogen-rich stream upstream of the second separator vessel.

An aspect of the invention further provides a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed, the cooling including feeding synthesis gas to a heat exchanger system in heat exchange relationship with an internal coolant stream that is produced subsequently in the process wherein the internal coolant stream is selected from the group consisting of a hydrogen rich vapour stream and a dense carbon dioxide stream,

b) passing the cooled stream formed in step (a) either directly or indirectly to a gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a dense CO_2 stream from separator vessel; and

d) feeding a hydrogen-rich stream to an expansion system including at least one

expander, preferably a plurality of expanders, and reducing the pressure of the hydrogen-rich gas at the or each expander.

Also provided by the invention is a system for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the system including:

a) a cooling system arranged to cool a gas stream to a temperature at which a two-phase mixture is formed,

b) a gas-liquid separator vessel arranged to receive the two-phase mixture either directly or indirectly from the cooling system, at a pressure of less than 150 bar, the output of the separator vessel being a hydrogen rich vapour stream and a liquid CO_2 stream; and

c) an expansion system arranged downstream of the separator vessel to receive a hydrogen rich vapour stream, the expansion system including a plurality of expanders arranged in series such that the hydrogen rich vapour stream is subjected to expansion in each of the expanders of the series such that a hydrogen rich vapour stream can be withdrawn from each of the expanders at reduced temperature and at successively reduced pressures

d) a flow path for feeding an expanded hydrogen rich stream to the cooling system.

Also provided by the invention is a system for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the system including:

a) a cooling system arranged to cool a synthesis gas stream to a temperature at which at which a two-phase mixture is formed,

b) a first gas-liquid separator vessel arranged to receive the cooled stream either directly or indirectly, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg, and to output a first hydrogen rich stream and a liquid CO_2 stream;

c) a second gas-liquid separator vessel downstream of the first separator for receiving the first hydrogen rich stream either directly or indirectly, and outputting a second hydrogen rich stream from the separator vessel and a liquid CO_2 stream from the separator vessel; and

d) an expansion system including at least one expander, arranged, preferably downstream of the second separator vessel, to receive a the hydrogen rich

vapour stream and subjected it to expansion in the expander of the system such that an expanded hydrogen rich vapour stream can be withdrawn from the expander at reduced temperature and at pressure; and

e) a flow path for feeding an expanded hydrogen-rich vapour stream to the cooling system.

The system may further include a compressor or pump arranged to increase the pressure of a separated carbon dioxide stream.

In some examples, the pressure at the separation step will be in the range 80 to 400bar, for example 80 to 250bar.

In some examples, an upstream shift reaction process may generate a shifted gas having a pressure in the range 50 to 100 bar. This shifted gas may in some examples be fed to the separation stage without significant change in the pressure of the stream. The shifted gas leaving a Water Gas Shift unit may for example be at a pressure in the range 50 to 100bar, for example 60 bar to 95 bar, for example 65 to 90 bar, in some examples 70 to 80 bar. The shifted gas in some examples may be at a pressure in the range 50 to 250 bar when cooled such that some preferably most of the carbon dioxide contained therein liquefies prior to separation. The pressure at the separation step may be 70bar, 75bar, or 80bar in some cases.

The synthesis gas stream preferably comprises a shifted syngas stream. The cooled stream fed to the separator vessel preferably comprises a shifted syngas. It will be appreciated that in some arrangements, one or more steps of the process may be carried out for example before or after the shifting step.

It has been found that the hydrogen rich vapour stream may be reduced in pressure to any desired pressure by passing the hydrogen enriched vapour stream through a turboexpansion system that comprises a plurality of turboexpanders arranged in series. In particular, the hydrogen rich vapour stream may be obtained at the desired fuel gas feed pressure for a combustor of a gas turbine of a power plant (for example, at a pressure of 30 barg). It has also been found that or more expanded H_2 rich vapour streams that exit each turboexpander of the series may be used as internal coolant streams thereby providing a portion, for example a major portion, of the refrigeration duty for the heat exchanger system. In some examples, expansion of the H_2 rich vapour in the turboexpanders may be used to drive a rotor or shaft of a compressor(s) of a compressor system (if present) or to

drive the rotor or shaft of a turbo-electric generator thereby achieving a reduction of the net power consumption for the separation of the synthesis gas stream into a hydrogen rich vapour stream and liquid CO_2 stream

The motive power generated in the turboexpanders may be used for example to drive a machine that is a component of the CO_2 condensation plant and/or to drive an alternator of an electric generator. The machine that is driven by a turboexpander may be a compressor in a compression system (for example a compression system used in the separation process, if required) and/or a pump.

In some examples, for example as described above, the pressure of the synthesis gas feed stream is at least 40 bar.

In particular in examples where a pressurised hydrogen enriched gas is advantageous, for example for use as a feed to a turbine, preferably the pressure of the synthesis gas feed stream in the process is at least 60 bar, for example at least 80 bar or more. The pressure of the stream fed to a separator vessel of the system may be for example 125 bar or less, for example 110 bar or less, 100 bar or less, or 90 bar.

In some examples, there will be a compression step required to compress the syngas, for example, the shifted syngas, to increase the pressure.

Thus the process may include the step of, prior to the separation, and preferably prior to the cooling using the internal coolant stream, compressing the synthesis gas using a compression system such that the gas is increased in pressure to a pressure in the range of 60bar to less than 150 bar. Preferably the method further includes the step of cooling the resulting high pressure gas against a coolant (for example an external refrigerant and/or internal cooling stream) to remove at least part of the heat of compression.

In other arrangements, the syngas feed, for example the shifted syngas feed, for example the feed from a Water Gas Shift apparatus, may be such that no further compression is required. Indeed, as described herein, the separation step may be carried out without significant, or any, compression being required upstream of the separation.

Thus yet a further aspect of the invention provides a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) feeding a synthesis gas stream to a cooling system, without substantially increasing the pressure of the synthesis gas stream immediately upstream of the

cooling system;

b) cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed, the cooling including feeding synthesis gas to a heat exchanger system, preferably in heat exchange relationship with an internal coolant stream that is produced subsequently in the process wherein the internal coolant stream is selected from the group consisting of a hydrogen rich vapour stream and a dense carbon dioxide stream,

c) passing the cooled stream formed in step (a) either directly or indirectly, with substantially no increase in pressure, to a gas-liquid separator vessel,

d) withdrawing a hydrogen rich vapour stream from the separator vessel and a dense CO_2 stream from separator vessel; and

e) feeding a hydrogen rich vapour stream to an expander system including one, preferably a plurality of expanders, wherein a hydrogen-rich stream is subjected to expansion in the or each expander.

Preferably the expanded hydrogen stream is cool and is used as a coolant in the system. Preferably a plurality of expanded hydrogen streams are used as coolant streams.

The method may include feeding a hydrogen rich vapour stream to a turboexpansion system including a plurality of turboexpanders arranged in series, wherein the hydrogen rich vapour stream is subjected to isentropic expansion in each of the turboexpanders of the series such that a hydrogen rich vapour stream is withdrawn from each of turboexpanders at reduced temperature and at successively reduced pressures and wherein isentropic expansion of the hydrogen rich vapour in each of the turboexpanders of the series generates motive power.

Thus preferably the native feed of synthesis gas, for example shifted synthesis gas fed for example from a Water Gas Shift system, is not further compressed prior to the separation of the carbon dioxide from the stream.

Thus according to some aspects of the invention, the first separation, and optionally subsequent separation steps, is carried out at substantially the pressure of the feed gas stream. For example, the feed gas pressure may be between 60bar and 125 bar, for example 60 bar to 100 bar.

The temperature of the cooled stream passed to the gas-liquid separator vessel will depend in part on the pressure of the stream in the case that it is required that a two-phase

mixture be formed. In examples, the temperature of the feed stream to the separator apparatus will generally be between -15 degrees C and -55 degrees C, preferably less than -30 degrees C, preferably less than -40 degrees C, preferably -50 degrees C or less.

Accordingly, a further aspect of the invention provides a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a synthesis gas stream having a pressure of less than 150 barg to a temperature between -15 degrees C and -55 degrees C, the cooling including feeding synthesis gas to a heat exchanger system in heat exchange relationship with an internal coolant stream that is produced subsequently in the process wherein the internal coolant stream is selected from the group consisting of a hydrogen rich vapour stream and a dense carbon dioxide stream,

b) passing the cooled stream formed in step (a) either directly or indirectly to a gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a dense CO_2 stream from separator vessel; and

d) preferably feeding a hydrogen rich vapour stream to a turboexpansion system including a plurality of turboexpanders arranged in series, wherein the hydrogen rich vapour stream is subjected to isentropic expansion in each of the turboexpanders of the series such that a hydrogen rich vapour stream is withdrawn from each of turboexpanders at reduced temperature and at successively reduced pressures and wherein isentropic expansion of the hydrogen rich vapour in each of the turboexpanders of the series generates motive power.

In some examples, all or substantially all of the cooling in step (a) may be carried out using one or more internal cooling streams. Alternatively, some cooling may additionally be provided using an external coolant or refrigerant. For example a refrigerant such as ethane or propane may be used, although other coolants and refrigerants are possible. Preferably cooling using external coolants, if any, is provided downstream of the internal cooling, but in other examples it may be preferred to provide external cooling upstream of

cooling using internal coolants, or between cooling stages using internal coolant.

Also provided by an aspect of the invention is provided a process for separating a synthesis gas stream into a hydrogen (H_2) rich vapour stream and a liquid carbon dioxide (CO_2) stream in a CO_2 condensation plant that comprises (a) a heat exchanger system, (b) a gas-liquid separator vessel, and (c) a turboexpansion system comprising a plurality of turboexpanders arranged in series, the process comprising the steps of:

(A) providing a feed synthesis gas stream having a pressure in the range of 10 to 120 barg;

(B) cooling the synthesis gas stream of step (A) to a temperature in the range of -15 to -55°C by passing the synthesis gas stream through the heat exchanger system in heat exchange relationship with a plurality of internal refrigerant streams wherein the internal refrigerant streams are selected from the group consisting of cold hydrogen rich vapour streams and liquid CO_2 streams;

(C) passing the cooled synthesis gas stream formed in step (B) either directly or indirectly to a gas-liquid separator vessel that is operated at substantially the same pressure as the heat exchanger system and withdrawing a hydrogen rich vapour stream from at or near the top of the separator vessel and a liquid CO_2 stream from at or near the bottom of the separator vessel; and

(D) feeding the hydrogen rich vapour stream from step (C) to the turboexpansion system wherein the hydrogen rich vapour stream is subjected to isentropic expansion in each of the turboexpanders of the series such that hydrogen rich vapour streams are withdrawn from the turboexpanders of the series at reduced temperature and at successively reduced pressures and wherein isentropic expansion of the hydrogen rich vapour in each of the turboexpanders of the series generates motive power thereby driving a machine that is a component of the CO_2 condensation plant and/or driving an alternator of an electric generator.

In some examples, it is preferred for the pressure of the stream at the gas-liquid separator vessel to be substantially the same as the pressure of the initial feed gas, thus for there to be no or substantially no pressurising of the gas between the feed and the separation step.

In other examples, preferably the system includes a compression system comprising at least one compressor, the feed gas being fed to the compression system such that the

synthesis gas is increased in pressure before the separation step. For example, the pressure may be increased to more than 60 bar, more than 70 bar, more than 80 bar or 100 bar or more. The process may further include cooling the resulting increased pressure synthesis gas stream, for example against an external coolant and/or external refrigerant to remove at least part of the heat of compression.

A multistage compression system may be preferred in some arrangements where compression is required, for example multistage compression may be preferred for higher discharge pressures from the compression system but is optional, in particular for lower discharge pressures from the compression system. Generally, the compressor(s) of any compression system used in the apparatus may be mounted on a shaft that may be driven by an electric motor, gas turbine or steam turbine. Alternatively, or in addition, compressor(s) of a compression system and turboexpanders of a turboexpansion system may be mounted on a common shaft so that the isentropic expansion of the hydrogen rich vapour in the turboexpanders may be used to drive the compressor(s).

A typical multistage compression system for use in the examples of the present invention may comprise at least one low pressure (LP) compressor, preferably two or three LP compressors mounted on a common drive shaft and at least one high pressure (HP) compressor, preferably one or two HP compressors mounted on a further common drive shaft (the drive shafts may be connected via a gear system). The LP and HP compressors are arranged in series. As would be well known to the person skilled in art, increased compression efficiency is achieved by balancing the compression duty across the compressors of the series. Thus, it is preferred that the compression ratios between successive compressors of the series be substantially the same.

In any of the aspects described herein, the separation process may be a single stage or multiple stage process. Further cooling stages may be provided between the separation stages. In some examples, after the final stage of a series of separation steps, the hydrogen-rich stream will be fed to an expansion device. Preferably the expansion device is adapted to reduce the pressure of the hydrogen-rich stream. Preferably the expansion is carried out such that the temperature of the gas stream is reduced. Preferably the expansion is carried out such that the reduction in pressure is recovered as work. For example the expansion may be carried out using a turboexpander, for example as described above.

Preferably, the cooled synthesis gas stream formed in a cooling step may be passed to a cryogenic separation system comprising at least one cryogenic separation stage wherein the cryogenic separation stage(s) is comprised of a heat exchanger that employs an external refrigerant and a gas-liquid separator vessel. Accordingly, the gas-liquid separator vessel employed in some examples of the present invention may be either the gas-liquid separator vessel of a single cryogenic separation stage that employs an external refrigerant or is the final gas-liquid separator vessel of a series of cryogenic separation stages wherein the cryogenic separation stages each employ an external refrigerant and are operated at progressively lower temperatures. In other examples, cooling will be provided alternatively, or in addition, using one or more streams of internal coolant.

An advantage of examples of the present invention is that at least 65%, for example at least 75%, and in some examples at least 90%, more preferably, at least 95% of the carbon dioxide may be separated from the synthesis gas feed stream with the carbon dioxide capture level being dependent upon the pressure of the synthesis gas stream, any increase of pressure in the system and on the temperature of the cooled gas, for example whether or not the cooled synthesis gas stream is subjected to cryogenic cooling against an external refrigerant. For example, it has been found that 75 to 85% of the CO_2 might be captured from the synthesis gas feed stream in some examples where an external refrigerant is not used.

It has been found for examples where the pressure at which the separation step is carried out at a pressure of less than about 80bar (including for example cases where no initial compression is carried out before the first separation step), the amount of captured CO_2 is generally between about 65 and 80 % mol. Where higher pressures are used (for example by including one or more compressors in the system), higher capture rates may be obtained.

The hydrogen rich vapour stream may be reduced in pressure, for example to the desired inlet pressure for the combustor(s) of the gas turbine(s). For example by isentropically expanding the hydrogen rich vapour stream, for example in one or a series of turboexpanders cold H_2 rich vapour streams (internal coolant or refrigerant streams) that may be used to cool the synthesis gas stream. In addition, isentropic expansion of the hydrogen rich vapour streams for example in each of the turboexpanders of the series can generate motive power that may be used to drive the compressor(s) of a compression

system (if present) and/or to drive at least one alternator of an electric generator thereby generating electricity for use in the process (for example, for operating one or more electric compressors of the compression system) and/or to drive a pump (for example, a pump for a liquid CO_2 or supercritical CO_2 stream). Thus, a major portion of the compression energy may be recovered using the turboexpanders thereby increasing the overall energy efficiency of the process.

It is recognised that the hydrogen rich vapour stream may be expanded to pressures below the inlet pressure of the combustor of a gas turbine, if the hydrogen rich vapour stream is to be used for a different purpose, for example, as fuel for a low pressure burner of a fired heater, or as fuel for a reformer or boiler or as a refinery feed stream for upgrading of one or more refinery streams or as a hydrogen feed to a chemical process.

The pressure drop across the heat exchanger system may be less than 1.5 bar.

In some preferred examples, the heat exchanger system comprises at least one multichannel heat exchanger and the synthesis gas stream is passed through a channel in the multichannel heat exchanger in heat exchange relationship with a plurality of internal refrigerant or coolant streams that are passed through further channels in the multichannel heat exchanger. The multichannel heat exchanger may be a diffusion-bonded heat exchanger, for example, a printed circuit heat exchanger.

The heat exchanger system may comprise a plurality of stand-alone heat exchangers arranged in series and the synthesis gas stream may be cooled as it is passed through the heat exchangers of the series by heat exchange with a plurality of internal refrigerant streams that are fed to the first and successive heat exchangers of the series at successively lower temperatures.

Typically, in examples of the invention, the heat exchanger system comprises at least one multichannel heat exchanger with the gas stream being passed through a channel of the multichannel heat exchanger in heat exchange relationship with a plurality of internal refrigerant/coolant streams that are passed through further channels in the multichannel heat exchanger. Representative examples of a multichannel heat exchanger include those described in US 6622519, WO 2004/016347, EP 212878 and EP 292245 the disclosures of which are incorporated herein by reference. As an alternative, or in addition to pre-cooling the synthesis gas stream against an external refrigerant in a heat exchanger of the compression system, it is envisaged that one or more external refrigerant streams may be

passed through yet further channels in the multichannel heat exchanger thereby providing additional cooling duty for the synthesis gas stream. Preferably, the synthesis gas stream is passed in a counter-current direction through the multichannel heat exchanger to the internal refrigerant streams and optional external refrigerant stream(s). Preferably in some examples, the heat exchanger system comprises a plurality of refrigeration stages arranged in series where each stage in the series comprises either (i) a single multichannel heat exchanger, or (ii) a plurality of multichannel heat exchangers arranged in parallel, for example, 2 or 3 multichannel heat exchangers arranged in parallel. For example, the heat exchanger system may comprise three refrigeration stages arranged in series with the internal refrigerant streams and optional external refrigerant stream(s) being fed to each successive stage of the series at successively lower temperatures. In an example of a heat exchanger system, a first refrigeration stage comprises two single-pass multichannel heat exchangers arranged in parallel, a second refrigeration stage comprises three 3-pass multichannel heat exchangers arranged in parallel, and a third refrigeration stage comprises a single 4-pass multichannel heat exchanger. Thus, the synthesis gas stream can be divided and recombined as it passes through the stages of the heat exchanger system thereby optimising the heat exchange with the internal refrigerant streams and/or external refrigerant stream(s). However, alternative arrangements for a plurality of multichannel heat exchangers may be adopted.

Alternatively, or in addition, the heat exchanger system may comprise a plurality of refrigeration stages wherein each refrigeration stage comprises either a single stand-alone heat exchanger or a plurality of stand-alone heat exchangers arranged in parallel. Thus, for example, the synthesis gas stream (or other stream) is cooled as it is passed through the refrigeration stages of the heat exchanger system by heat exchange with a plurality of internal refrigerant streams and optional external refrigerant stream(s) that are fed to the stand-alone heat exchanger(s) of each successive refrigeration stage at successively lower temperatures. It is preferred that the synthesis gas stream is passed through the stand-alone heat exchangers in a counter-current direction to the internal refrigerant streams and optional external refrigerant stream(s) that are fed to the stand-alone heat exchangers.

It is also envisaged that the heat exchanger system may comprise both multichannel and stand-alone heat exchangers. Thus, the heat exchanger system may comprise a plurality of refrigeration stages arranged in series wherein each refrigeration stage

comprises (i) a single multichannel heat exchanger, or (ii) a single stand-alone heat exchanger, or (iii) a plurality of multichannel heat exchangers and/or a plurality of stand-alone heat exchangers arranged in parallel.

The multichannel heat exchanger(s) of the heat exchanger system may be of the type employed in processes for generating liquefied natural gas such as a brazed aluminium plate-fin heat exchanger or a diffusion-bonded heat exchanger (for example, a printed circuit heat exchanger (PCHE) as supplied by Heatric). Alternatively, the multichannel heat exchanger(s) may be a multiple body shell and tube heat exchanger comprising either (a) a tube arranged in the shell of the heat exchanger wherein the shell of the heat exchanger comprises a plurality of compartments and wherein the synthesis gas stream is passed through the tube and an internal refrigerant stream or external refrigerant stream is passed through each compartment of the shell in heat exchange relationship with the synthesis gas that is flowing through the tube; or (b) a plurality of tubes arranged in the shell of the heat exchanger wherein the shell comprises a single compartment and the synthesis gas is passed through the compartment and an internal refrigerant stream or an external refrigerant stream is passed through each of the tubes in heat exchange relationship with the synthesis gas that is flowing through the single compartment of the shell. Accordingly, the term "channel" encompasses the channels formed between the plates of a brazed aluminium plate-fin heat exchanger or a diffusion-bonded heat exchanger and also the compartment(s) and tube(s) of a multiple body shell and tube heat exchanger.

The stand-alone heat exchanger(s) of the compression system may be of the shell and tube type (a single body shell and tube heat exchanger) with the synthesis gas stream passing through the tube side and an internal refrigerant stream or external refrigerant stream passing through the shell side of the heat exchanger or vice versa. However, a process that employs stand-alone heat exchangers to pre-cool the synthesis gas stream may be of reduced efficiency compared with a process that employs a multichannel heat exchanger, in whole or in part, to cool the synthesis gas stream in step (B) of the present invention.

The cooled stream that exits the heat exchanger system is a two phase stream comprised of a liquid phase and vapour phase. There is generally a practical limit on the temperature to which the gas stream may be cooled in the heat exchanger system as the

temperature should normally be maintained above a value where solid CO_2 will form. This typically occurs at a temperature of -56°C (the triple point for pure CO_2 is at 5.18 bar and at a temperature of -56.4°C) although the presence of H_2 may depress this freezing point. The amount of cooling that is achieved in the heat exchanger system owing to heat exchange with the plurality of internal refrigerant streams will be dependent upon the amount of cooling of the isentropically expanded hydrogen rich vapour streams that is achieved in the turboexpansion system which, in turn, is dependent on the pressure of the hydrogen rich vapour stream that is formed and the pressure of the H_2 rich vapour stream that exits a turboexpander or a final turboexpander of the turboexpansion system. The amount of electricity generated by turboexpanders of a turboexpansion system will also be dependent on the extent to which the hydrogen rich vapour is subjected to isentropic expansion in the turboexpansion system which is also dependent on the pressure of the H_2 rich vapour stream formed and the pressure of the H_2 rich vapour stream that exits the final turboexpander of the turboexpansion system.

The term "refrigerant" used herein preferably includes any appropriate coolant where appropriate.

Preferably the term "external refrigerant" includes a refrigerant that is formed in an external refrigeration circuit. Accordingly, liquid CO_2 that is formed in the process of the present invention is not regarded as an external refrigerant. Suitable external refrigerants that may be used as refrigerant in the heat exchanger(s) include propane, ethane, ethylene, ammonia, hydrochlorofluorocarbons (HCFCs) and mixed refrigerants. Typical mixed refrigerants comprise at least two refrigerants selected from the group consisting of butanes, propanes, ethane, and ethylene. These refrigerants may be cooled to the desired refrigeration temperature in external refrigerant circuits using any method known to the person skilled in the art including methods known in the production of liquefied natural gas (LNG) or natural gas liquids (NGLs).

These refrigerants may also be cooled to the desired refrigeration temperature for example by heat exchange with one or more cold isentropically expanded H_2 rich vapour streams from the turboexpanders of the turboexpansion system. The external refrigerant for the cryogenic separation stage is selected so as to achieve the desired operating temperature. For example, propane may be used as refrigerant when the feed temperature of the gas stream is in the range of -15 to greater than -30°C and the desired operating

temperature of the cryogenic separation stage is in the range of -20 to greater than -30°C while ethane and/or ethylene may be used as external refrigerant when the feed temperature of the gas stream is in the range of -30 to -40°C and the desired operating temperature for the cryogenic separation stage is in the range of -40 to -55°C, preferably, -45 to -50°C. Other arrangements are possible

The CO_2 stream that is withdrawn from the gas-liquid separator may in some examples be obtained at the liquid CO_2 export pressure and the liquid CO_2 stream may be passed through the heat exchanger system, for example in heat exchange relationship with the synthesis gas stream before being exported from the process and sequestered and/or used in a chemical process.

The CO_2 stream may in some examples be obtained at a pressure above the liquid CO_2 export pressure and is reduced in pressure to the liquid CO_2 export pressure before being passed to a flash separation vessel where a hydrogen rich vapour stream is withdrawn from at or near the top of the flash separation vessel and a liquid CO_2 stream is withdrawn from at or near the bottom of the flash separator vessel and the liquid CO_2 stream is then passed through the heat exchanger system in heat exchange relationship with the synthesis gas stream before being exported from the process and sequestered and/or used in a chemical process.

However, in many examples of aspects of the present invention, the CO_2 is withdrawn from the separator vessel at a pressure which is less than a required export pressure. For example, in accordance with some aspects of the invention, the pressure of the separated CO_2 is less than 150 bar, for example less than 120 bar, less than 100 bar, less than 80 bar or even less. Therefore in some arrangements, the method further includes the step of pressurizing the separated CO_2, for example using a pump, although other appropriate apparatus could be used, for example a compressor. The pressure to which the CO_2 is pressurised will of course depend on its intended usage, but in some examples, preferably the pressure of the pressurised CO_2 is more than 100 bar, more than 120 bar, preferably 150 bar or more.

Treatment of the liquid carbon dioxide recovered will depend on its intended use. It may for example be piped or transported off-site for underground storage. The liquid carbon dioxide may if desired be warmed by passing it through one or more of the cooling stages, for example one or more of the multichannel heat exchangers to utilise its cooling

capacity also.

While the carbon dioxide withdrawn in the separation stage will be in the liquid phase, it will be understood that carbon dioxide elsewhere in the process may be in a supercritical dense phase. For example, when the liquid carbon dioxide is warmed as suggested above, the temperature of the carbon dioxide may rise above the critical temperature. References herein to liquid carbon dioxide should be construed accordingly.

The hydrogen rich vapour stream that is withdrawn from the flash separation vessel may be combined with a hydrogen rich vapour stream of similar pressure that is withdrawn from one of the turboexpanders and/or is combined with a synthesis gas feed stream of similar pressure that is obtained by passing the synthesis gas feed stream through a compression system (if present).

The hydrogen rich vapour stream that exits the final turboexpander may be obtained at a pressure in the range of 25 to 45 barg, preferably, 30 to 35 barg and may be passed as fuel gas to a combustor of at least one gas turbine of a power plant.

The cooled synthesis gas stream cooled in the heat exchanger may have a temperature in the range of -30 to -40°C and may be subsequently passed to a cryogenic separation system that comprises a single cryogenic separation stage comprised of a heat exchanger that employs an external refrigerant and a gas-liquid separator vessel wherein the pressure drop across the cryogenic separation stage is preferably in the range of 0.1 to 5 bar; the heat exchanger of the cryogenic separation stage preferably has an operating temperature in the range of -40 to -55°C; and wherein the hydrogen rich vapour stream and the liquid CO_2 stream are withdrawn from the gas-liquid separator vessel of the cryogenic separation stage.

The cooled synthesis gas stream may have a temperature in the range of -15 to -30°C and may be passed to a cryogenic separation system comprising a plurality of cryogenic separation stages that are arranged in series wherein each cryogenic separation stage of the series is comprised of a heat exchanger that employs an external refrigerant and a gas-liquid separation vessel; the cryogenic separation stages of the series are operated at progressively lower temperatures and with a pressure drop across the series of cryogenic separation stages preferably in the range of 0.1 to 5 bar; the hydrogen rich vapour stream and the liquid CO_2 stream being withdrawn from the gas-liquid separator vessel of the final cryogenic separation stage in the series; and additional HP liquid CO_2 streams being

withdrawn from each of the preceding cryogenic separation stages in the series.

Where the process includes the step of compressing the synthesis gas, preferably synthesis gas is compressed in a multistage compressor system comprising a plurality of compressors arranged in series wherein a heat exchanger is provided after each compressor of the series and wherein the synthesis gas is preferably cooled in each heat exchanger against an external coolant for example selected from the group consisting of air, water or a against cold process stream selected from the H_2 rich vapour stream and the final H_2 rich vapour stream.

The synthesis gas feed stream may be a sour synthesis gas stream comprising H_2S wherein a major portion of the H_2S partitions into the liquid CO_2 phase and is sequestered with the liquid CO_2 stream(s) and residual H_2S in the final H_2 rich vapour stream may be removed downstream of the CO_2 condensation plant for example by passing the final H_2 rich vapour stream through a bed comprising a particulate adsorbent material or through a scrubber wherein the H_2 rich vapour stream contacts a liquid absorbent.

The CO_2 product stream may be used as injection fluid for an oil reservoir, for example by injecting the liquid CO_2 down an injection well and into the oil reservoir thereby displacing hydrocarbons towards an associated production well.

Also provided by an aspect of the invention is a carbon dioxide condensation plant for separating carbon dioxide and hydrogen from a synthesis gas stream, the plant comprising:

(a) a source of a synthesis gas feed stream;

(b) optionally a compression system;

(c) a heat exchanger system arranged to cool the (optionally compressed) synthesis gas stream against at least one (preferably a plurality of) internal coolant or refrigerant streams thereby partially condensing the synthesis gas stream;

(d) a gas-liquid separator vessel arranged to receive the partially condensed synthesis gas stream; and

(e) a turboexpander system comprising a plurality of turboexpanders arranged in series to receive a hydrogen rich vapour stream from the gas-liquid separator vessel, a turbo expander being arranged to expand a hydrogen rich vapour stream and to feed the expanded hydrogen rich vapour stream to the heat exchanger system.

In preferred arrangements, the apparatus includes means (for example an expander)

for reducing the pressure of the H_2-rich fraction downstream of the separator stage. Preferably the apparatus is arranged such that the expanded H_2-rich fraction is subsequently used as an internal coolant elsewhere in the apparatus or in a related apparatus. Where the apparatus includes a plurality of expanders, preferably the apparatus is such that the H_2-rich fraction is used as a coolant after each expansion step, although other arrangements are of course possible. Preferably the expander is such that it recovers work in expanding the hydrogen-rich gas.

In any of the examples described herein, and any of the aspects of the invention as appropriate, other process steps may be included, and further components included in the system as required. For example, the process may include a solvent separation stage, for example to remove CO_2, H_2S or other component from one or more streams. For example, prior to expansion, H_2 rich vapour stream may be fed to a solvent extraction system in which the vapour stream is contacted with a solvent which absorbs residual CO_2 contained therein. Solvent extraction processes for effecting this separation include the Rectisol™ and Selexol™ processes which respectively use refrigerated methanol and a refrigerated mixture of dimethyl ethers of polyethylene glycol as the absorbent. Alternatively the absorbent can be amine based for example monoethanolamine, diethanolamine, methyldiethanolamine diisopropylamine or the like. Any other appropriate method may be used. Alternatively, or in addition, solvent separation stage(s) may be included at other parts of the system.

As discussed above, the hydrogen enriched synthesis gas vapour stream may be used as fuel gas for the combustor of the gas turbine(s). It is preferred that the fuel gas contains 35 to 65 mole % hydrogen, more preferably, 45 to 60 mole % hydrogen, for example, 48 to 52 mole % of hydrogen. An advantage of the present invention is that the hydrogen enriched synthesis gas vapour stream that is discharged from the cryogenic separation plant contains CO_2 as a co-component. It may therefore not be necessary to add a diluent such as nitrogen and/or steam to the hydrogen enriched synthesis gas vapour stream in order to meet the fuel specification for the combustor of the gas turbine. Alternatively, the amount of diluent added to the hydrogen enriched synthesis gas vapour stream may be reduced.

The exhaust gas from the gas turbine(s) is passed to a heat recovery and steam generator unit (HRSG) where the exhaust gas may be heat exchanged with various process streams. Optionally, the temperature of the exhaust gas from the gas turbine is increased

by providing the HRSG with a post-firing system, for example, a post-firing burner. Suitably, the post-firing burner is fed with a portion of the hydrogen enriched synthesis gas fuel stream which is combusted in the burner using residual oxygen contained in the exhaust gas. Suitably, the exhaust gas is raised in temperature in the post-firing system to a temperature in the range of 500 to 800°C.

Typically, the HRSG generates and superheats steam for use in at least one steam turbine and elsewhere in the process of the present invention. Typically, the HRSG is capable of generating high pressure (HP) steam, medium pressure (MP) steam and low pressure (LP) steam and of superheating these steam streams. The HRSG may also be capable of reheating MP steam that is produced as an exhaust stream from the high pressure stage of a multistage steam turbine. In addition, the HRSG may be used to heat boiler feed water (for example, boiler feed water that is fed to the waste heat boiler of a shift converter unit).

The cooled exhaust gas is discharged from the HRSG to the atmosphere through a stack. Preferably, the stack is provided with a continuous emission monitoring system for monitoring, for example, the NO_x content of the cooled exhaust gas.

The liquid CO_2 stream(s) that are withdrawn from the separator vessel(s) of the cryogenic separation stage(s) preferably comprises at least 90 mole% CO_2, in particular, at least about 94 mole % CO_2, the remainder being mostly hydrogen with some inerts, for example, nitrogen and/or CO. Where the cryogenic separation plant comprises a plurality of cryogenic separation stages arranged in series, the liquid CO_2 streams that are withdrawn from the stages are preferably combined. The liquid CO_2 stream or combined liquid CO_2 stream is preferably fed to a to a rectification column for removal of residual hydrogen. Typically, the rectification column is a distillation column comprising a plurality of distillation trays, for example, 3 to 5 distillation trays. The liquid CO_2 stream or combined liquid CO_2 stream is fed to an intermediate position in the column while a hydrogen enriched vapour stream is withdrawn from at or near the top of the distillation column and a liquid CO_2 stream having a reduced content of hydrogen is removed from at or near the bottom of the distillation column. Typically, the liquid CO_2 stream that is removed from at or near the bottom of rectification column has a hydrogen content of less than 1% by volume, preferably, less than 0.05% by volume. Preferably, the distillation column is operated with reflux i.e. the hydrogen enriched vapour stream that is withdrawn

from at or near the top of the distillation column is cooled to below its dew point against an external refrigerant, for example, propane or ethane, to condense out liquid CO_2 and the condensed liquid CO_2 is returned to the upper part of the column, for example, to the top tray of the column.

The liquid CO_2 stream is then pumped to the desired export pressure, for example, the pipeline delivery pressure. The liquid CO_2 stream may then be transferred by pipeline to a reception facility of an oil field where the stream may be used as an injection fluid in the oil field. If necessary, the liquid CO_2 stream is further pumped to above the pressure of an oil reservoir before being injected down an injection well into the oil reservoir. The injected CO_2 displaces the hydrocarbons contained in the reservoir rock towards a production well for enhanced recovery of hydrocarbons therefrom. If any carbon dioxide is produced from the production well together with the hydrocarbons, the carbon dioxide may be separated from the hydrocarbons for re-injection into the oil reservoir such that the CO_2 is sequestered in the oil reservoir. It is also envisaged that the liquid CO_2 stream may be injected into an aquifer or a depleted oil or gas reservoir for storage therein.

According to the invention there is also provided a method and/or apparatus being substantially as herein described, preferably having reference to one or more of the accompanying drawings.

Any one or more of the features described herein may be combined in any appropriate combination. Features of one aspect of the invention may be combined, where appropriate, with features of another aspect of the invention. Method features may be provided as apparatus features, and vice versa.

Examples of processes and/or apparatus of aspects of the present invention will now be illustrated by reference to the following Figures.

Figure 1 shows a block flow diagram that illustrates the production of a synthesis gas stream comprising hydrogen and carbon dioxide and the separation of a hydrogen enriched synthesis gas stream from a carbon dioxide stream using a cryogenic separation plant.

Figure 2 provides a more detailed view a cryogenic separation plant according to the present invention while

Figure 3 relates to a cryogenic separation plant according to a preferred embodiment of the present invention.

Figures 4a and 4b show the external refrigeration circuits that produce the external

refrigerants for the cryogenic separation plants of Figures 2 and 3.

Figure 5 shows schematically elements of a further example of a system for use in a method of separation of carbon dioxide from a synthesis gas;

Figure 6 shows schematically elements of a further example of a system for use in a method of separation of carbon dioxide from a synthesis gas.

In Figure 1, a shifted synthesis gas stream comprising 30 to 65 mole % H_2, 35 to 70 mole % CO_2, up to 3 mole % of CO, and up to 100 ppm of H_2S, is subjected to Low Temperature Gas Cooling to knock out water contained in the shifted synthesis gas stream. Typically, this is achieved by cooling the shifted synthesis gas stream to a temperature of approximately 30 to 40°C in a heat exchanger against boiler feed water thereby generating steam. Cooling results in condensation of the majority of the water which is separated in a knockout drum. In practice, cooling of the shifted synthesis gas stream generates two steam streams, low pressure (LP) steam and medium pressure (MP) steam. These steam streams may be used in an upstream plant (for example, a gasifier) or sent to a steam turbine for electricity generation. The water that is separated in the knock-out drum will contain trace amounts of CO_2 and other impurities. These impurities are stripped from the condensate in a Condensate Stripper. The remaining condensate (water) is then used as boiler feed water.

The shifted synthesis gas from the Low Temperature Gas Cooling Stage may then sent to an Acid Gas Removal (AGR) plant where the H_2S may be stripped out of the CO_2 enriched stream via the use of a physical or chemical absorbent in an absorption tower. Typically Selexol™ (a mixture of dimethyl ethers of polyethylene glycol) is used as absorbent. The separated H_2S may be passed to a Claus plant for the production of elemental sulphur, or may be converted to sulphuric acid in a sulphuric acid plant. However, where it is desired to co-capture the H_2S, the shifted synthesis gas from the Low Temperature Gas Cooling Stage an AGR plant may be eliminated with the H_2S partitioning into the liquefied CO_2 in the separator vessel(s) of the cryogenic separation stage(s) of the plant. If necessary, the hydrogen enriched synthesis gas vapour stream that is separated from the captured CO_2 and co-captured H_2S is passed through a zinc oxide guard bed to remove any residual H_2S prior the stream being used as a fuel gas. Alternatively, H_2S may be removed from the cold hydrogen enriched synthesis gas vapour stream downstream of the single cryogenic separation stage or stage N of the series, using a chemical absorbent in

an absorption tower, for example, Rectisol® (methanol). Typically, an absorption tower that employs Rectisol® as absorbent is operated at a temperature of about -40°C. Accordingly, the hydrogen enriched synthesis gas vapour stream should be passed to the absorption tower, prior to the vapour stream being heated to above -40°C against the dried synthesis gas feed stream.

The synthesis gas feed stream that exits the AGR plant (or by-passes the AGR plant) is then dried, as any moisture in the synthesis gas feed stream will cause freezing and blockages in downstream processing equipment. Viable options for dehydrating the synthesis gas feed stream include passing the gas through a molecular sieve bed. Typically, the water content of the dried synthesis gas feed stream is less than 1 ppm (molar basis).

Once dehydrated, the synthesis gas feed stream is sent at a pressure of 57 bar to a cryogenic separation plant. This cryogenic separation plant typically comprises a multichannel heat exchanger and at least one, preferably, two or more cryogenic separation stages arranged in series. In the multichannel heat exchanger, the synthesis gas feed stream is cooled against one or more cold product streams. However, it is also envisaged that the multichannel heat exchanger may be replaced by two or more shell and tube heat exchangers arranged in series and/or in parallel that each employ a cold product stream as coolant for the synthesis gas feed stream. Where the shell and tube heat exchangers are employed in parallel, the synthesis gas feed stream is divided and a portion of the feed stream is sent to each heat exchanger and the cooled streams are subsequently recombined downstream of the heat exchangers.

Where there is a single cryogenic separation stage, the synthesis gas feed stream is cooled to below its dew point against an external refrigerant in a heat exchanger of the single separation stage that is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 55 to 59 bar absolute so that the stream becomes two phase (a liquid phase comprising substantially liquid CO_2 and a vapour phase that is enriched in H_2 compared with the synthesis gas feed stream). The liquid phase is then separated from the vapour phase in a separator vessel of the single cryogenic separation stage and a liquid CO_2 stream and a hydrogen enriched synthesis gas vapour stream are removed from at or near the bottom and top of the separator vessel respectively. Where two or more cryogenic separation stages are arranged in series, the cryogenic separation stages will separate at

least two liquid CO_2 streams from the hydrogen enriched synthesis gas vapour stream that is discharged from the final stage of the series. Thus, the synthesis gas feed stream is cooled to below its dew point against an external refrigerant in a heat exchanger of a first cryogenic separation stage of the cryogenic separation plant so that the stream becomes two phase. The liquid phase (substantially pure liquid CO_2) is then separated from the vapour phase in a separator vessel of the first cryogenic separation stage and a liquid CO_2 stream and a hydrogen enriched synthesis gas vapour stream are removed from at or near the bottom and top of the separator vessel respectively. The hydrogen enriched synthesis gas vapour stream is then further cooled to below its dew point against a further external refrigerant in a heat exchanger of the second stage of the cryogenic separation plant so that the stream becomes two phase and a liquid phase (substantially pure liquid CO_2) is then separated from a vapour phase (that is further enriched in hydrogen) in a separator vessel of the second stage. This may be repeated using further cryogenic separation stages until a sufficient level of CO_2 capture has been achieved. However, the final stage of the series should be operated at a temperature in the range of -53 to -48°C and a pressure in the range of 55 to 59 bar absolute. An advantage of removing a liquid CO_2 stream from each cryogenic separation stage of the series is that this reduces the refrigeration load for the subsequent cryogenic separation stage(s) of the series by minimizing sub-cooling of the liquid. Thus, the liquid CO_2 stream that is removed from the first and intermediate cryogenic separation stages of the series by-passes the subsequent separation stage(s) and is therefore not subjected to additional cooling.

Where there is a single cryogenic separation stage, ethane and/or ethylene is generally used as refrigerant thereby allowing cooling of the synthesis gas feed stream to a temperature in the range of -53 to -48°C.

Where there are two or more cryogenic separation stages arranged in series, propane may be used as refrigerant in one or more cryogenic separation stages followed by the use of ethane and/or ethylene as refrigerant in one or more further cryogenic separation stages, depending on the desired condensation temperatures in the different cryogenic separation stages. However, other refrigerants may be used such as ammonia, hydrochlorofluorocarbons (HCFC's) and mixed refrigerants. Typical mixed refrigerants comprises at least two refrigerants selected from the group consisting of butanes, propanes, ethane, and ethylene.

Where the cryogenic separation plant comprises a single cryogenic separation stage, the liquid CO_2 stream is passed to a pump that increases the pressure of the stream for transportation. Where the cryogenic separation plant comprises a plurality of cryogenic separation stages arranged in series, the liquid CO_2 streams that are withdrawn from the separation vessels of the cryogenic stages of the plant are combined before being passed to a pump that increases the pressure of the combined liquid CO_2 stream for transportation.

The H_2 enriched synthesis gas vapour stream that is discharged from the single cryogenic separation stage or from the last cryogenic separation stage (Stage N) of the series comprises between 75 and 90 mole% H_2 and between 10 and 25 mole% CO_2. This H_2 enriched synthesis gas vapour stream is at a high pressure (typically, approximately 59 barg) as the pressure drop across the cryogenic separation stages are ideally minimised . The hydrogen enriched synthesis gas vapour stream is then reduced in pressure before being passed to the inlet of the gas turbines (GTs) of the Power Island, preferably, using one or more turboexpanders. It will generally be necessary to warm the hydrogen enriched synthesis gas vapour stream before it enters the turboexpander(s) so as to mitigate the risk of a fall in temperature to below the temperature at which solid CO_2 would form in the turboexpander(s). Typically, the hydrogen enriched synthesis gas may be warmed by being passed through the multichannel heat exchanger before entering the turboexpander(s). The expansion energy recovered from the H_2 enriched synthesis gas vapour stream in the turboexpander(s) can be converted into electrical power for export or for use within the plant (e.g. to drive the CO_2 pumps or the compressor(s) of the external refrigeration circuit(s)). Isentropic expansion of the hydrogen enriched synthesis gas vapour stream in the turboexpander(s) results in cooling of the hydrogen enriched synthesis gas vapour stream. As discussed above, advantageously, the hydrogen enriched synthesis gas vapour stream(s) that exit the turboexpander(s) may be used to cool the synthesis gas feed stream in the multichannel heat exchanger or in two or more shell and tube heat exchanger(s).

The expanded hydrogen enriched synthesis gas vapour stream is then sent to a Fuel Gas Saturation and Dilution Stage (saturation tower) where the hydrogen enriched synthesis gas vapour stream is diluted with steam and/or optionally nitrogen thereby generating a fuel stream comprising approximately 50 mole % hydrogen. Dilution of the fuel stream may be required in order to control NO_X emissions and flame speeds.

However, the presence of CO_2 in the fuel stream may reduce or even eliminate the need for added diluent. The fuel stream is then sent to the Power Island, where the fuel is combusted in air in the combustor of at least one modified gas turbine (GT). The GT can be used to drive an electric motor thereby generating electricity. The exhaust gas from the gas turbine is passed to a Heat Recovery Steam Generator (HRSG) where the exhaust gas is heat exchanged with boiler feed water thereby generating steam and/or with steam to generate superheated steam. Typically, three levels of steam (HP, MP or LP) can be generated from boiler feed water. The resulting steam streams may be combined with the petroleum coke or coal that is fed to the gasifier and/or may be used in a steam turbine that drives an electric generator thereby producing additional electricity. The exhaust gas from the HRSG is vented to atmosphere.

Figure 2 shows a detailed process flow diagram for the cryogenic separation plant of the block diagram outlined in Figure 1. A synthesis gas feed stream 1 is fed at a pressure of 57 bar absolute to a cryogenic separation plant. The synthesis gas feed stream 1 comprises hydrogen (for example, 40 to 65 mole %, typically 55 mole %), carbon dioxide (for example, 35 to 60 mole %, typically 45 mole %), and contaminants such as water, inerts (for example nitrogen and/or argon), methane and carbon monoxide. Where the synthesis gas feed stream is obtained from a high pressure coal or petroleum coke gasifier, it may be a sour shifted synthesis gas stream comprising hydrogen sulfide (0.2 to 1.5 mole %, typically about 1 mole %). Where the shifted synthesis gas stream is derived from a reformer, hydrogen sulfide will have been removed from the feed to the reformer so as to avoid poisoning the reforming catalyst. Accordingly, the synthesis gas feed stream will not contain any hydrogen sulfide impurity.

Where the synthesis gas feed stream 1 is a sour synthesis gas stream, the synthesis gas feed stream may be sent on to an Absorption Tower (C-101), where the stream 1 is contacted with a solvent that acts as a selective absorbent for H_2S thereby generating a desulfurised synthesis gas stream 2. Suitable solvents that can act as selective absorbent for H_2S include physical solvents, for example, Selexol™ (a mixture of dimethyl ethers of polyethylene glycol) or chemical solvents, for example, methyldiethylamine (MDEA). However, the desulfurised synthesis gas stream 2 may still retain trace amounts of H_2S.

Optionally, the desulfurised synthesis gas stream 2 is then cooled in heat exchanger E-107 against propane refrigerant thereby generating a cold stream 2A. It is important that

the cold stream 2A is maintained at a temperature above 0° in order to avoid the deposition of ice in the plant. The cooled synthesis gas stream 2A that exits heat exchanger E107 is then sent to drier D-500 in order to remove water prior to condensing out the CO_2 in a cryogenic separation plant. There are many methods known in the art for the removal of saturated water from a process stream including absorbent beds (for example, molecular sieve beds). The resulting dried synthesis gas stream 3 enters the cryogenic separation plant at an elevated pressure of 57 barg and at a temperature above 0°C. If the plant does not include optional heat exchanger E-107, the temperature of the dried synthesis gas stream is typically slightly above ambient, for example, 20 to 45°C. The dried synthesis gas stream is then cooled in multichannel heat exchanger EX-101, for example, a plate fin heat exchanger, against a plurality of cold process streams (see below) thereby generating a cooled synthesis gas feed stream 4 having a pressure of 56 bar absolute and a temperature of, for example, approximately -27°C. Accordingly, a portion of the CO_2 in the cooled synthesis gas feed stream that exits multichannel heat exchanger EX-101 will separate as a liquid phase from a vapour phase. Optionally, a separator vessel may be provided upstream of the first cryogenic separation stage to remove this condensed liquid phase.

The cooled shifted synthesis gas feed stream 4 then enters the first of a series of three cryogenic separation stages each of which comprises a heat exchanger and separator vessel. The separator vessels (V-102, V-103 and V-104) are operated at substantially the same pressure but at successively lower temperatures. In heat exchanger E-102 of the first cryogenic separation stage, the cooled synthesis feed stream 4 is further cooled to a temperature of -29.7°C against propane refrigerant to generate a two phase stream 5 which is then passed to separator vessel V-102 where a portion of the CO_2 in stream 5 separates as a liquid phase from a vapour phase. A vapour stream 6 that is enriched in hydrogen and depleted in CO_2 is removed overhead from separator vessel V-102 and is passed through heat exchanger E-103 where it is further cooled against propane or ethane refrigerant to a temperature of -40.8°C thereby generating a further two phase stream 8 which is passed to separator vessel V-103 where a portion of the CO_2 in stream 8 separates as a liquid phase from a vapour phase. A vapour stream 9 that is further enriched in hydrogen is withdrawn overhead from separator vessel V-103 and is passed through heat exchanger E-104 where this stream is further cooled to a temperature of -50°C against ethane refrigerant thereby generating a two phase stream 11 that is passed to separator vessel V-104 where a portion

of the CO_2 in stream 11 separates as a liquid phase from a vapour phase. A hydrogen enriched synthesis gas stream 12 is discharged overhead from separator vessel V-104.

The propane refrigerant that is fed to the shell side of heat exchangers E-107, and E-102 and the ethane refrigerant that is fed to the shell side of heat exchangers E-103 and E-104 is at successively lower temperatures and may be obtained using any cryogenic method known to the person skilled in the art, including cryogenic methods for producing refrigerants for liquefying natural gas. The ethane refrigerant for heat exchangers E-103 and E-104 may be replaced with ethylene. In addition, the refrigerant for each of the heat exchangers E-107, and E-102 to E-104 may be replaced with a mixed refrigerant stream comprising at least two refrigerants selected from the group consisting of butanes, propanes, ethane and ethylene. The composition of the mixed refrigerant streams that are fed to the different heat exchangers may be adjusted to achieve the desired level of cooling.

Although the process of the invention has been described with respect to 3 cryogenic separation stages, the number of cryogenic separation stages may be increased or decreased depending predominantly on the different levels of refrigeration being used, the desired level of carbon capture, energy efficiency targets and the capital cost requirements. Preferably, at least 2 cryogenic separation stages are provided. There is a limit on the lowest temperature in the last stage of separation, as the temperature must be maintained above a value where solid CO_2 will form. This typically occurs at a temperature of -56°C (the triple point for pure CO_2 is at 5.18 bar and at a temperature of 56.4°C) although the presence of H_2S may depress this freezing point. Accordingly, the temperature of the last cryogenic separation stage should be above -55°C, preferably, -53 to -48°C. The pressure of the final cryogenic separation stage is maintained as high as possible in order to ensure the highest possible capture of CO_2. Typically, the pressure drop across the cryogenic separation stages of the plant is at least 1 bar, for example, 1 to 5 bar. Accordingly, the pressure of the final cryogenic separation stage may be up to 55 bar absolute.

The liquid CO_2 streams 7, 10 and 13 from the separation vessels V-102, V-103, and V-104 respectively are at substantially the same pressure and are mixed to generate a combined stream 14 that is sent to a separation vessel V-107. A liquid CO_2 stream 16 is withdrawn from the bottom of vessel V-107 and is sent to CO_2 pump P-101. The CO_2 pump P-101 increases the pressure of the CO_2 to the pipeline export pressure, of approximately 130 to 200 barg. The high pressure liquid CO_2 stream 17 is then passed

through the multichannel heat exchanger E-101 before being passed to a further separator vessel V-101 where a liquid CO_2 stream 71 is withdrawn from at or near the bottom of vessel V-101 and is sent to pipeline

Any vapour leaving overhead from vessel V-107 is combined with stream 12 upstream of multichannel heat exchanger E-101 thereby generating stream 55 . Stream 55 is then passed through multichannel heat exchanger E-101 where it is used to precool the dried synthesis gas feed stream 3. The hydrogen enriched synthesis gas stream 56 that exits the multichannel heat exchanger E-101 is combined with a hydrogen enriched vapour stream 67 that is withdrawn overhead from separator vessel V-101 thereby forming stream 68 which is optionally diluted with medium pressure steam to form diluted stream 69. Stream 69 is then passed through heat exchanger E-401 before being sent as a fuel gas stream 70 to a power plant (not shown). The purpose of heat exchanger E-401 is to raise the temperature of the diluted stream 69 to the desired feed temperature for the GTs of the power plant.

Figure 3 illustrates a modification to the cryogenic separation plant described in Figure 2. In Figure 3, the combined liquid CO_2 stream 66 that exits multichannel heat exchanger E-101 is passed to a rectification column T-101 for removal of residual hydrogen from the liquid CO_2 stream. The combined liquid CO_2 stream 66 is fed to an intermediate position in the column while a hydrogen enriched vapour stream 67 is withdrawn from at or near the top of the distillation column and a liquid CO_2 stream 71 having a reduced content of hydrogen is removed from at or near the bottom of the distillation column and is sent to a pipeline. Also, in Figure 3, the hydrogen enriched synthesis gas vapour stream 12 that is discharged overhead from separator vessel V-104 is passed through a channel of the multichannel heat exchanger E-101 where it is used to cool the dried synthesis gas feed stream 3. The hydrogen enriched synthesis gas vapour stream that exits the multichannel heat exchanger is at a pressure of about 55 barg and a temperature of about -10°C and is fed to turboexpander K-101 where it is expanded to the pressure of the hydrogen enriched synthesis gas vapour stream 15 that is withdrawn overhead from separator vessel V-107 thereby resulting in cooling of the stream. The expanded hydrogen enriched synthesis gas vapour stream exits the turboexpander K-101 at a pressure of about 42 bara and a temperature of about -30°C and is then passed through a further channel in the multichannel heat exchanger where it provides additional cooling for

the dried synthesis gas feed stream 3. The expanded stream that exits the multichannel heat exchanger E-101 is then combined with stream 15 and the resulting combined stream is fed to turboexpander K-102 where it is expanded to a pressure of 32 bara and a temperature of - 30°C. The cooled stream that exits turboexpander K-102 is then passed through yet a further channel of the multichannel heat exchanger E-101 thereby providing additional cooling for the dried synthesis gas feed stream 3. The expanded hydrogen enriched synthesis gas vapour stream 56 that exits the multichannel heat exchanger is then combined with the hydrogen enriched synthesis gas vapour stream 67 that is withdrawn overhead from rectification column T-101 thereby forming stream 68.

The propane refrigerant, for use in the cryogenic condensation plants of Figures 2 and 3, is compressed in three stages by a centrifugal compressor K-301, as shown in Figure 4a.

Propane vapour stream 301 from the compressor K-301 discharge is desuperheated in the air cooled Desuperheater E-301 and is then fully condensed in air cooled Condenser E-302. The liquefied propane 305 is collected in a horizontal propane receiver, V-301. A liquid propane stream is withdrawn from the bottom of V-301 and a first portion 306 of this liquid propane stream is routed to HP heat exchanger E-107 (upstream of drier D-500). A second portion 320 of this liquid propane stream is reduced in pressure across a valve and is fed to vessel V-302. A liquid propane stream is withdrawn from the bottom of vessel V-302 and is reduced in pressure across a further valve thereby forming stream 310 which is fed to vessel V-303. A liquid propane stream 334 that is withdrawn from the bottom of vessel V-303 is divided to form streams 334A and 349 that are routed to the heat exchanger (kettle) E-102 of the first cryogenic separation stage and the ethane refrigerant circuit condenser E-201A-D. The vapour stream 308 exiting the top of heat exchanger E-107 and the vapour stream 322 exiting the top of vessel V-302 are combined to form stream 308B which is routed to the propane compressor K-301 via propane compressor suction drum V-306 and line 311. The vapour stream exiting the top of vessel V-303 is routed to the propane compressor K-301 via propane compressor suction drum V-305 and the propane vapour exiting the top of heat exchanger E-102 and ethane refrigerant circuit condenser E-201A-D is routed to the propane compressor K-301 via propane compressor suction drum V-304. Propane compressor suction drums V-306, V-305 and C304 are at successively lower pressures.

The Ethane refrigerant in the CO_2 Condensation Circuit is compressed in two stages

by centrifugal compressors K-201 and K-202 that operate on a common shaft, as shown in Figure 4b. Ethane vapour streams 210 and 216 from the discharge of the compressors are combined to form stream 201 that is fully condensed against propane refrigerant in Ethane Condenser E-201A-D. The liquefied ethane stream 204 exiting E-201 is then collected in a horizontal ethane receiver, V-201. The discharge pressure of the compressors is governed by the condensing pressure at the exit of the Ethane Condenser E-201A-D.

The condensed ethane liquid (stream 205) is routed to the heat exchangers (kettles) E-103 and E-104 of the second and third cryogenic separation stages in the HP and LP ethane circuit loops respectively. For the HP ethane circuit loop, ethane flow to kettle E-103 (stream 207) is controlled by means of an inlet level control valve. The vapour stream 208 exiting the E-103 kettle is routed to the HP Ethane compressor K-201 via the HP ethane suction drum V-202 and line 209. For the LP ethane circuit loop, ethane flow is via an Ethane Economiser E-202 to the E-104 kettle, again controlled by means of a kettle inlet level control valve. The vapour stream 213A exiting the E-104 kettle is routed to the LP Ethane compressor K-202 via the Ethane Economiser E-202, to recover the cooling duty, and a LP ethane suction drum V-203.

Figure 5 shows a further example of a system for use in a method of separating carbon dioxide from a synthesis gas.

In an example of a method using the arrangement in Figure 5, a dry, H_2S-free syngas feed stream 1 containing about 55.6 mol% H_2, and 42.7 mol% CO_2 in addition to other components including CO, CH_4, N_2 and at a temperature of 40 degrees C and pressure of 57 bar is split into two streams 2 and 4.

Stream 2 is then cooled against external coolant or external refrigerant in heat exchanger E1 to bring the temperature of stream 3 to about -41 degrees C, and stream 4 is cooled in heat exchanger LNG2 against H_2 and CO_2-containing product streams 6 and 9 to bring the temperature of stream 5 to about -41 degees C. Streams 3 and 5 are mixed to form S1.

Stream S1 enters heat exchanger LNG1 and undergoes further cooling against internal product streams to bring stream S2 to a temperature of -50 degrees C.

The two-phase mixture in stream S2 is then separated in separation vessel V1 into a carbon dioxide-rich liquid stream S2L including 98.1 mol% CO_2 and capturing 72.4% of the CO_2 in the feed stream 1, and a hydrogen-rich vapor stream SV2 including 80.3 mol%

H_2 and less than 17 mol% CO_2 and recovering 98.9% of the H_2 in the feed stream 1.

Using the CO_2 stream S2L as an internal coolant in heat exchanger LNG1 raises the temperature of CO_2 stream 8 to approximately -38 degrees C, the pressure of the CO_2 liquid stream is boosted in pump P1 to bring the pressure of stream 9 to about 150 bar and achieve the required export pressure in this example for CO_2 storage. It will be understood that in other applications, a different export pressure for CO_2 storage may be desirable. The liquid CO_2 is used as an internal coolant in heat exchanger LNG2 bringing the temperature of stream 10 to approximately 35 degrees C.

The hydrogen rich vapor in stream S2V is used as an internal coolant in heat exchanger LNG1 and then fed via line 1N to series of turboexpanders EX1 and EX2 where it is progressively expanded isentropically to lower pressure producing mechanical work to aid the compression of feed synthesis gas. The person skilled in the art will understand that isentropic expansion of this gas stream will result in it being cooled. Accordingly the hydrogen-rich gas exits EX1 at a pressure of 42 bar and a temperature of -53 degrees C and is routed through heat exchanger LNG1 where it is heat exchanged with the high pressure gas stream S1 to bring stream 2N up to a temperature of approximately -38 degrees C and then passed to turboexpander EX2 where it is expanded yet again to form stream 2T at a pressure of 32bar and a temperature of -53 degrees C and is again routed through heat exchanger LNG1 where it is heat exchanged with the high pressure gas stream S1 to bring stream 6 up to a temperature of approximately -38 degrees C. Stream 6 enters LNG2 where it exchanges heat with stream 4 to produce stream 7 exiting the apparatus at a temperature of approximately 35 degrees C, and a pressure of 30 bar which is a suitable temperature and pressure for a fuel feed for a turbine power generator in this example.

Figure 6 shows a further example of a system for use in a method of separating carbon dioxide from a synthesis gas.

In an example of a method using the arrangement in Figure 6, a dry, H_2S-free syngas feed stream 1 containing about 55.6 mol% H_2, and 42.7 mol% CO_2 in addition to other components including CO, CH_4, N_2 is fed to compressor C1 at a temperature of 40 degrees C and pressure of 57 bar. This stream 1 is compressed in two stages with intercooling to bring the pressure of stream 2D to 120bar and then cooled in E2 to bring the temperature of stream 3 to 40 degrees C.

Stream 3 is then cooled against external coolant or external refrigerant in heat

exchanger E3 before entering heat exchanger LNG1 where the stream S1 is further cooled against internal product streams to bring stream S2 to a temperature of -50 degrees C to form a two-phase mixture. In the present example, there may be for example a small pressure drop within the heat exchangers so that the pressure is reduced for example to about 118 bar.

Stream S2 is then separated in separator V1 into a carbon dioxide-rich liquid stream S2L including 97.3 mol% CO_2 and capturing 83.6% of the CO_2 in stream 1, and a hydrogen-rich vapor stream S2V including 86.2 mol% H_2 and recovering 97.3% of the H_2 in stream 1.

Using the CO_2 stream S2L as an internal coolant in heat exchanger LNG1 raises the temperature of stream 5 to approximately 10 degrees C, the pressure of the CO2 stream is then boosted in pump P1 to bring the pressure of stream 6 to 150 bar and achieve the required export pressure for CO_2 storage.

The hydrogen rich vapor in stream S2V is used as an internal coolant in heat exchanger LNG1 and then fed via line 1N to series of turboexpanders EX1, EX2 and EX3 where it is progressively expanded isentropically to lower pressure producing mechanical work to aid the compression of feed synthesis gas. The person skilled in the art will understand that isentropic expansion of this gas stream will result in it being cooled. Accordingly the hydrogen-rich gas exits EX1 at a pressure of 77 bar and a temperature of -53 degrees C and is routed through heat exchanger LNG-1 where it is heat exchanged with the high pressure gas stream S1 to bring stream 2N up to a temperature of approximately -30 degrees C and then passed to turboexpander EX2 where it is expanded yet again to form stream 2T at a pressure of 50bar and a temperature of -53 degrees C and is again routed through heat exchanger LNG-1 where it is heat exchanged with the high pressure gas stream S1 to bring stream 3N up to a temperature of approximately -30 degrees C and then passed to turboexpander EX3 where it is expanded yet again to form stream 3T at a pressure of 32bar and a temperature of -53°C and is again routed through heat exchanger LNG-1 where it is heat exchanged with the high pressure gas stream S1 to produce stream 4 exiting the apparatus at a temperature of +10 degrees C, and a pressure of 30 bar which is a suitable temperature and pressure for a fuel feed for a turbine power generator in this example.

It is to be understood that aspects of the invention are not limited to the examples

described herein, and various may be made within the scope of the invention.

In summary, a process is described for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant. In an example described the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to a single stage or a first stage of a series of separation stages at a pressure in the range of 46 to 90 bar absolute. The single stage or a stage of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to 90 bar absolute. In some examples, the single stage or the combined stages of the series remove 70 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream. Liquefied CO_2 product stream(s) discharged from the stage(s) of the cryogenic separation plant may be sequestrated and/or used in a chemical process.

Also described is a process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream. In an example, the process includes the steps of cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed, passing the cooled stream formed either directly or indirectly to a gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg, withdrawing a hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from the separator vessel; and feeding a separated hydrogen rich vapour stream to an expansion system including a plurality of expanders arranged in series, wherein the hydrogen rich vapour stream is subjected to expansion in each of the expanders of the series such that an expanded hydrogen rich vapour stream is withdrawn from each of the expanders at reduced temperature and at successively reduced pressures; and using at least one expanded hydrogen-rich vapour stream as a coolant.

Claims:

1. A process for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant that comprises either a single cryogenic separation stage or at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, the single stage or each stage of the series comprising the steps of (a) condensing carbon dioxide from the synthesis gas by cooling the synthesis gas by non-contact heat exchange with an external refrigerant to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the synthesis gas, with the single separation stage discharging a liquefied carbon dioxide product stream and a hydrogen enriched synthesis gas stream or, with each of the stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a hydrogen enriched synthesis gas vapour stream, characterized in that:

(i) the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to the single stage or the first stage of the series at a pressure in the range of 46 to 76 bar absolute;

(ii) the single stage or stage N of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to 74 bar absolute such that the single stage or the combined stages of the series remove 70 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream; and

(iii) the liquefied CO_2 product stream(s) discharged from the stage(s) of the cryogenic separation plant is sequestrated and/or used in a chemical process.

2. A process as claimed in Claim 1 wherein the liquid CO_2 product stream(s) is used for enhanced oil recovery before being sequestered.

3. A process as claimed in Claims 1 or 2 wherein 75 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream is separated in the cryogenic separation plant.

4. A process as claimed in any one of the preceding claims wherein the synthesis gas stream comprises hydrogen, carbon dioxide, and hydrogen sulfide and the hydrogen sulfide

is condensed from the synthesis gas stream in the single cryogenic separation stage or each of the cryogenic separation stages of the series and the hydrogen sulfide is removed from the single stage or each of the stages of the series in the liquefied carbon dioxide product stream(s).

5. A process as claimed in Claim 4 wherein the single stage or the combined stages of the series remove 80 to 90% of the total moles of hydrogen sulfide from the synthesis gas feed stream.

6. A process as claimed in any one of the preceding claims wherein the synthesis gas feed stream is cooled upstream of the cryogenic separation plant to a temperature in the range of 20 to 50°C thereby condensing out a condensate and the condensate is separated from the cooled synthesis gas stream.

7. A process as claimed in Claim 6 wherein the synthesis gas feed stream is dried prior to being passed to the CO_2 condensation plant such that the synthesis gas feed stream has a water content of less than 1 ppm on a molar basis.

8. A process as claimed in any one of the preceding claims wherein the synthesis gas feed stream is passed to a pre-cooling heat exchanger of the CO_2 condensation plant where the synthesis gas feed stream is pre-cooled against a cold process stream selected from a liquid CO_2 product stream and a cold H_2 enriched synthesis gas vapour stream.

9. A process as claimed in Claim 8 wherein the synthesis gas feed stream is pre-cooled in a multichannel heat exchanger by passing the synthesis gas feed stream through at least one channel of the multichannel heat exchanger and a plurality of cold process streams through further channels of the multichannel heat exchanger.

10. A process as claimed in any one of the preceding claims wherein the pressure drop across the single stage or the series of stages of the cryogenic separation plant is in the range of 2 to 10 bar.

11. A process as claimed in any one of the preceding claims wherein the hydrogen enriched synthesis gas vapour stream that exits the separator of the single cryogenic separation stage or that exits stage N of the series of cryogenic separation stages is passed through a channel of the multichannel heat exchanger in heat exchanger relationship with the synthesis gas feed stream and is then cooled by expansion to lower pressure in a first turboexpander before being fed to a further channel in the multichannel heat exchanger and the hydrogen enriched vapour stream is optionally cooled by expansion to a lower pressure

in a second turboexpander before being fed to a further channel of the multichannel heat exchanger thereby pre-cooling the synthesis gas feed stream to a temperature in the range of -15 to -35°C.

12. A process as claimed in Claim 11 wherein the hydrogen enriched synthesis vapour stream discharged from the single cryogenic separation stage or the final cryogenic separation stage (Stage N) of the cryogenic separation plant comprises at least 70 mole % hydrogen, preferably, at least 80 mole % hydrogen and the expanded hydrogen enriched vapour stream is used as a fuel stream for the combustor of a gas turbine that drives an electric generator thereby producing electricity provided that the hydrogen enriched vapour stream is not expanded to a pressure below the desired fuel gas feed pressure for the combustor.

13. A process as claimed in any one of the preceding claims wherein the liquid CO_2 stream that is removed from the single cryogenic separation stage or the combined liquid CO_2 stream that is removed from the series of cryogenic separation stages comprises at least 90 mole% CO_2, in particular, at least about 94 mole % CO_2, the liquid CO2 stream or combined liquid CO2 stream is fed to a rectification column and a liquid CO2 product stream comprising less than 1% by volume hydrogen is removed from at or near the bottom of the rectification column.

14. A process as claimed in any one of the preceding claims wherein the liquefied CO_2 product stream is transferred by pipeline to a reception facility of an oil field or gas field where the CO2 product stream is injected into a reservoir of the oil field or gas fluid.

15. A process for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a synthesis gas stream to a temperature at which at which a two-phase mixture is formed,

b) passing the cooled stream formed in step (a) either directly or indirectly to a gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from the separator vessel; and

d) feeding a separated hydrogen rich vapour stream to an expansion system including a plurality of expanders arranged in series, wherein the hydrogen rich

vapour stream is subjected to expansion in each of the expanders of the series such that an expanded hydrogen rich vapour stream is withdrawn from each of the expanders at reduced temperature and at successively reduced pressures; and

e) using at least one expanded hydrogen-rich vapour stream as a coolant.

16. A method according to claim 15, wherein the expanded hydrogen-rich vapour stream is used to cool one or more streams selected from a hydrogen-rich gas stream, a carbon dioxide stream and a synthesis gas stream.

17. A method according to claim 15 or claim 16, wherein the expanders effect isentropic expansion of the hydrogen rich vapour in each of the expanders of the series and generate motive power.

18. A method according to any of claims 15 to 17, further including increasing the pressure of the separated carbon dioxide stream.

19. A method according to any of claims 15 to 18, further including passing the separated hydrogen rich stream directly or indirectly to a further gas-liquid separator vessel and withdrawing a second separated hydrogen rich vapour stream from the separator vessel and a second liquid CO_2 stream from the separator vessel.

20. A process for separating a gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the process including the steps of:

a) cooling a gas stream to a temperature at which at which a two-phase mixture is formed,

b) passing the cooled stream formed in step (a) either directly or indirectly to a first gas-liquid separator vessel, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg

c) withdrawing a hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from separator vessel;

d) passing the hydrogen rich vapour stream formed in step (c) either directly or indirectly to a second gas-liquid separator vessel, and withdrawing a second hydrogen rich vapour stream from the separator vessel and a liquid CO_2 stream from the separator vessel; and

e) feeding a separated hydrogen rich vapour stream to an expansion system including at least one expander, wherein the hydrogen rich vapour stream is

subjected to expansion in the expander of the system such that an expanded hydrogen rich vapour stream is withdrawn from the expander at reduced temperature and at pressure; and

f) using an expanded hydrogen-rich vapour stream as a coolant.

21. A method according to claim 19 or claim 20, further including cooling the separated hydrogen-rich stream upstream of the second separator vessel.

22. A process for removing carbon dioxide from a synthesis gas feed stream in a cryogenic separation plant that comprises either a single cryogenic separation stage or at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, the single stage or each stage of the series comprising the steps of (a) condensing carbon dioxide from the synthesis gas by cooling the synthesis gas by non-contact heat exchange with an external refrigerant to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the synthesis gas, with the single separation stage discharging a liquefied carbon dioxide product stream and a hydrogen enriched synthesis gas stream or, with each of the stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a hydrogen enriched synthesis gas vapour stream, wherein:

(i) the synthesis gas feed stream comprises 40 to 65 mole % hydrogen and is fed to the single stage or the first stage of the series at a pressure in the range of 46 to 90 bar absolute;

(ii) the single stage or stage N of the series is operated at a temperature in the range of -53 to -48°C and a pressure in the range of 44 to 90 bar absolute such that the single stage or the combined stages of the series remove 70 to 80% of the total moles of carbon dioxide in the synthesis gas feed stream; and

(iii) the liquefied CO_2 product stream(s) discharged from the stage(s) of the cryogenic separation plant is sequestrated and/or used in a chemical process.

23. A process as claimed in any one of the preceding claims wherein the synthesis gas feed stream is passed to a heat exchanger system where the synthesis gas feed stream is against a colder process stream selected from a liquid CO_2 product stream and a H_2

enriched stream, and preferably the synthesis gas feed stream is cooled in a multichannel heat exchanger by passing the synthesis gas feed stream through at least one channel of the multichannel heat exchanger and a plurality of colder process streams through further channels of the multichannel heat exchanger.

24. A process as claimed in claim 23 wherein a hydrogen enriched gas vapour stream that exits the separator is passed through a channel of a multichannel heat exchanger in heat exchanger relationship with the synthesis gas feed stream and is then cooled by expansion to lower pressure in a first turboexpander before being fed to a further channel in the multichannel heat exchanger and the hydrogen enriched vapour stream is optionally cooled by expansion to a lower pressure in a second turboexpander before being fed to a further channel of the multichannel heat exchanger.

25. A process as claimed in any preceding claim wherein the hydrogen -rich stream is used as a fuel stream for the combustor of a gas turbine.

26. A process as claimed in any one of the preceding claims wherein the liquefied CO_2 product stream is transferred by pipeline to a reception facility of an oil field or gas field where the CO2 product stream is injected into a reservoir of the oil field or gas fluid.

27. A process for removing carbon dioxide from a gas feed stream in a cryogenic separation plant that comprises either a single cryogenic separation stage or at least two cryogenic separation stages arranged in series, with the stages in the series being designated stage 1 through stage N, the letter N representing the number of stages in the series, the single stage or each stage of the series comprising the steps of (a) condensing carbon dioxide from the gas by cooling the gas by non-contact heat exchange with a refrigerant to produce liquefied carbon dioxide, and (b) separating the liquefied carbon dioxide from the gas or, with each of the stages in the series cooling the synthesis gas to a successively lower temperature as the synthesis gas progresses from stage 1 to stage N, thereby separately removing a liquefied carbon dioxide product stream from each of the stages, with stage N discharging a gas vapour stream.

28. A system for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the system including:

a) a cooling system arranged to cool a gas stream to a temperature at which a two-phase mixture is formed,

b) a gas-liquid separator vessel arranged to receive the two-phase mixture either

directly or indirectly from the cooling system, at a pressure of less than 150 bar, the output of the separator vessel being a hydrogen rich vapour stream and a liquid CO_2 stream; and

c) an expansion system arranged downstream of the separator vessel to receive a hydrogen rich vapour stream, the expansion system including a plurality of expanders arranged in series such that the hydrogen rich vapour stream is subjected to expansion in each of the expanders of the series such that a hydrogen rich vapour stream can be withdrawn from each of the expanders at reduced temperature and at successively reduced pressures

d) a flow path for feeding an expanded hydrogen rich stream to the cooling system.

29. A system for separating a synthesis gas stream into a hydrogen rich vapour stream and a carbon dioxide rich stream, the system including:

a) a cooling system arranged to cool a synthesis gas stream to a temperature at which at which a two-phase mixture is formed,

b) a first gas-liquid separator vessel arranged to receive the cooled stream either directly or indirectly, the feed to the gas-liquid separator vessel having a pressure of less than 150 barg, and to output a first hydrogen rich stream and a liquid CO_2 stream;

c) a second gas-liquid separator vessel downstream of the first separator for receiving the first hydrogen rich stream either directly or indirectly, and outputting a second hydrogen rich stream from the separator vessel and a liquid CO_2 stream from the separator vessel; and

d) an expansion system including at least one expander, arranged, preferably downstream of the second separator vessel, to receive a the hydrogen rich vapour stream and subjected it to expansion in the expander of the system such that an expanded hydrogen rich vapour stream can be withdrawn from the expander at reduced temperature and at pressure; and

e) a flow path for feeding an expanded hydrogen-rich vapour stream to the cooling system.

30. A system according to claim 28 or claim 29, further including a compressor or pump arranged to increase the pressure of a separated carbon dioxide stream.

31. A process or a step of a process being substantially as herein described, optionally having reference to one or more of the accompanying figures.

32. A system or component of a system being substantially as herein described optionally having reference to one or more of the accompanying figures.

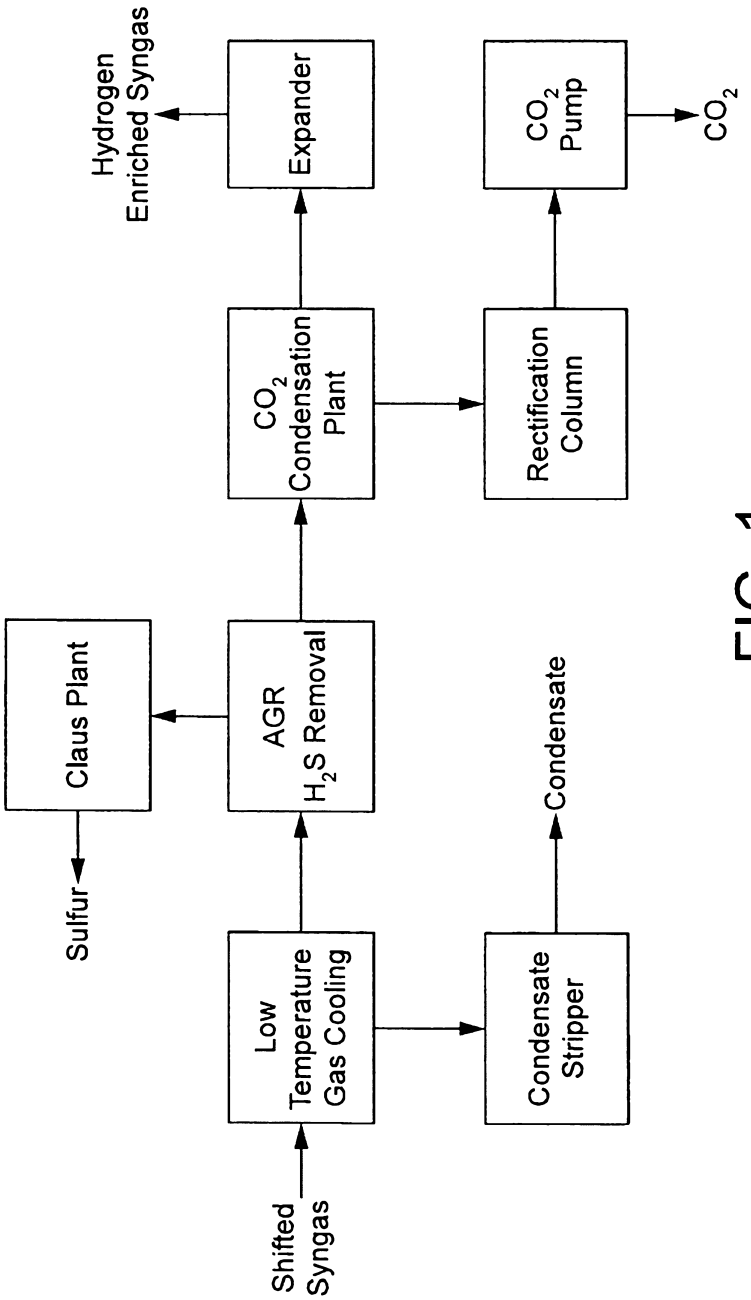
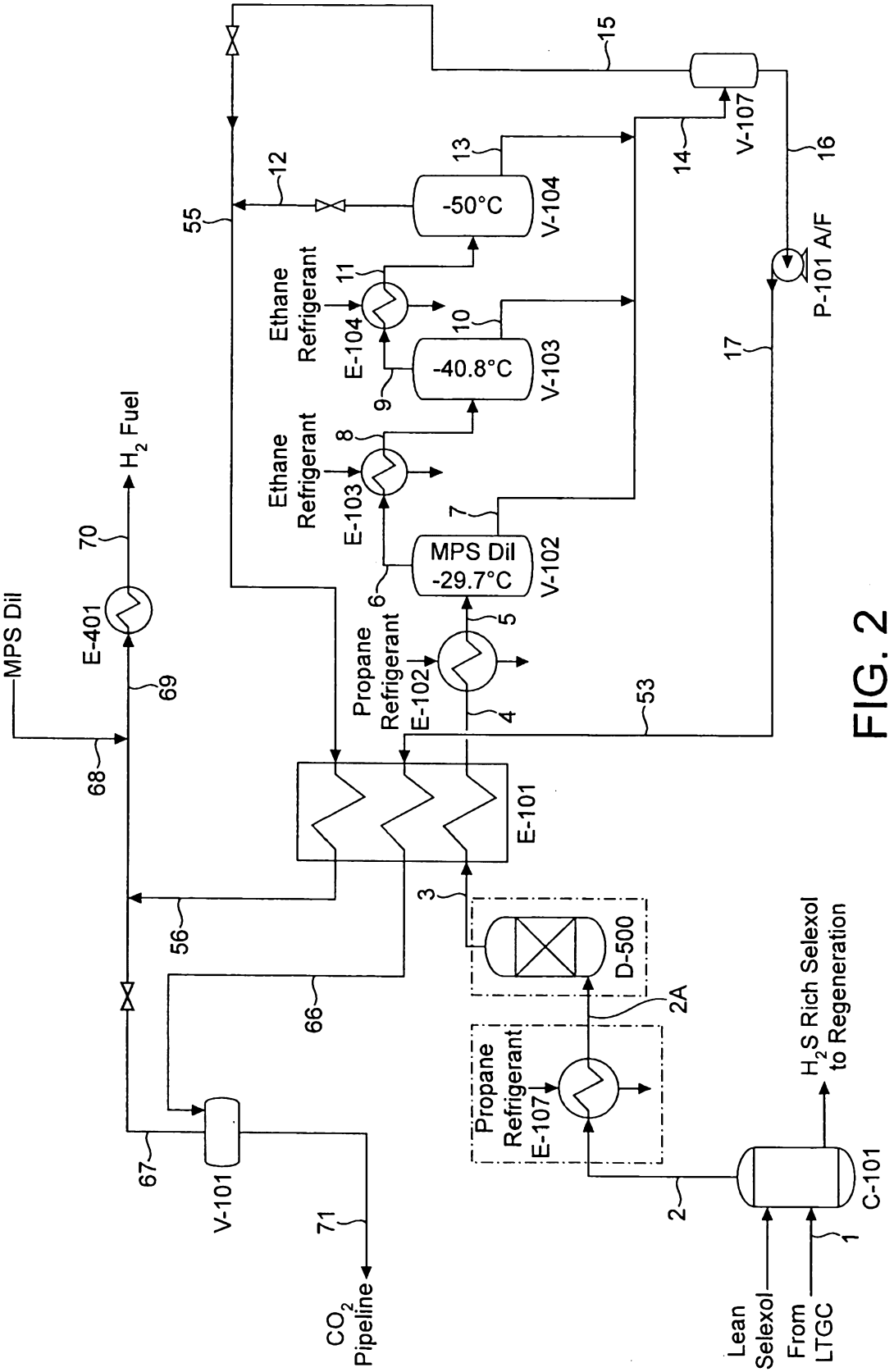

Hydrogen Enriched Syngas
Expander
CO_2 Pump
CO_2
CO_2 Condensation Plant
Rectification Column
Claus Plant
AGR H_2S Removal
Sulfur
Low Temperature Gas Cooling
Condensate Stripper
Condensate
Shifted Syngas

FIG. 1


Lean Selexol From LTGC
C-101
H_2S Rich Selexol to Regeneration
Propane Refrigerant E-107
D-500
2A
E-101
Propane Refrigerant E-102
MPS Dil -29.7°C V-102
Ethane Refrigerant E-103
-40.8°C V-103
Ethane Refrigerant E-104
-50°C V-104
V-107
P-101 A/F
E-401
H_2 Fuel
MPS Dil
V-101
CO_2 Pipeline
1
2
3
4
5
6
7
8
9
10
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13
14
15
16
17
53
55
56
66
67
68
69
70
71

FIG. 2

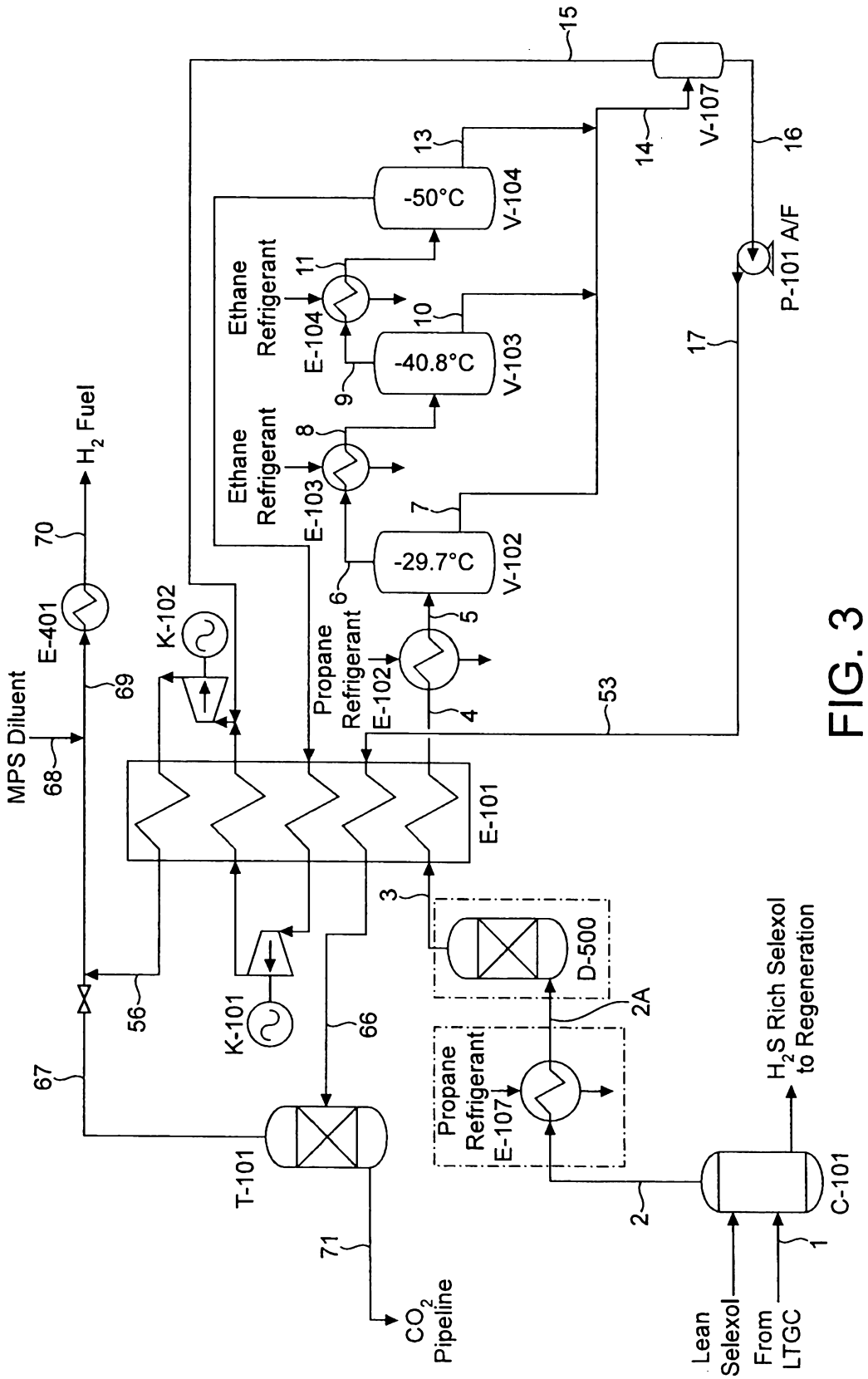
Lean Selexol From LTGC
1
C-101
2
H_2S Rich Selexol to Regeneration
2A
D-500
3
Propane Refrigerant E-107
T-101
71
CO_2 Pipeline
66
67
56
K-101
MPS Diluent
68
69
E-401
70
H_2 Fuel
K-102
E-101
Propane Refrigerant E-102
4
5
-29.7°C V-102
6
7
Ethane Refrigerant E-103
8
-40.8°C V-103
9
10
Ethane Refrigerant E-104
11
-50°C V-104
13
14
V-107
15
16
P-101 A/F
17
53

FIG. 3

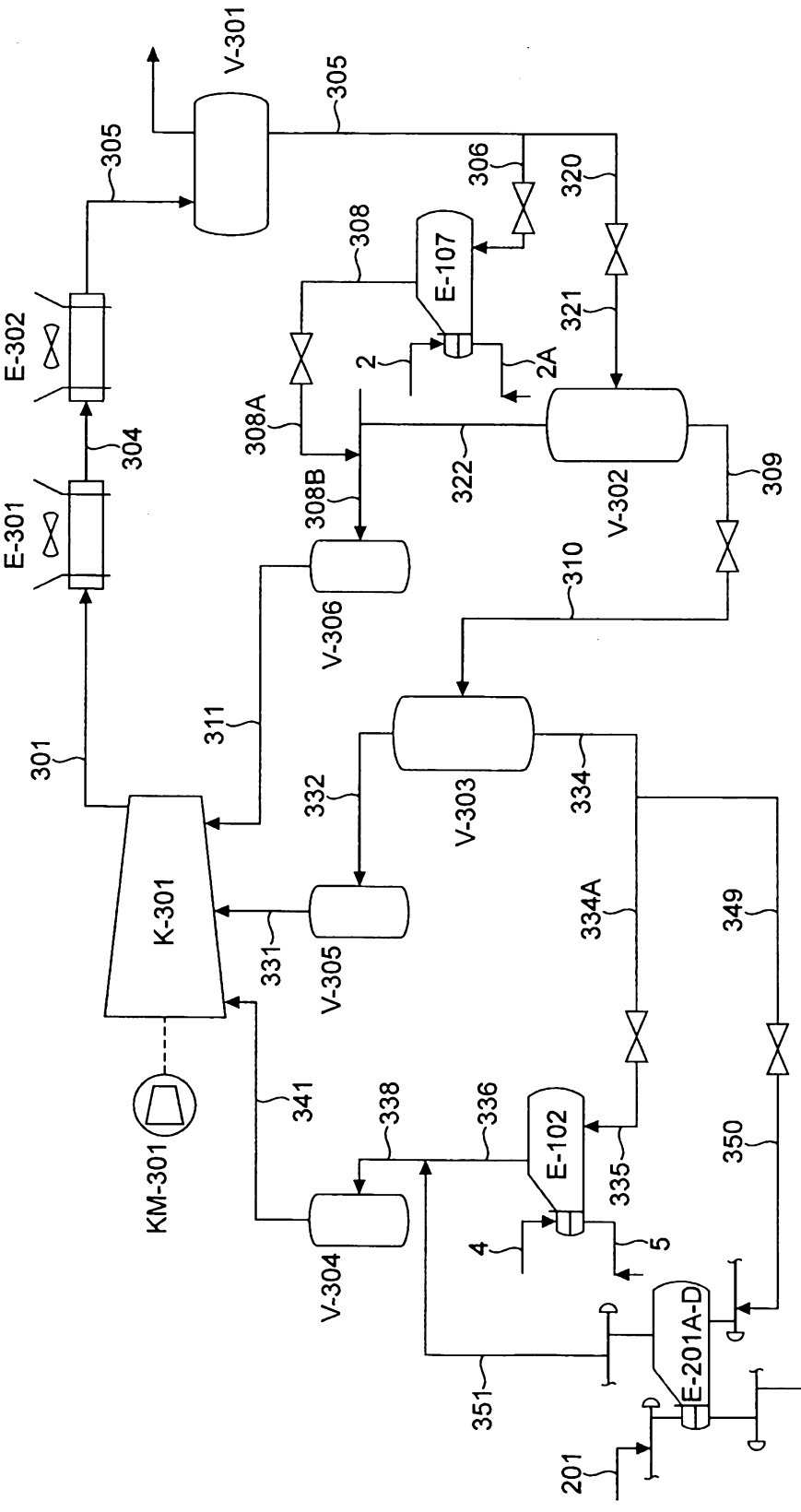
V-301
305
305
306
320
308
E-107
321
E-302
2
2A
308A
304
322
V-302
309
E-301
308B
V-306
310
311
301
332
V-303
334
K-301
334A
349
331
V-305
KM-301
341
338
336
E-102
335
350
4
5
V-304
E-201A-D
204
351
201

FIG. 4a

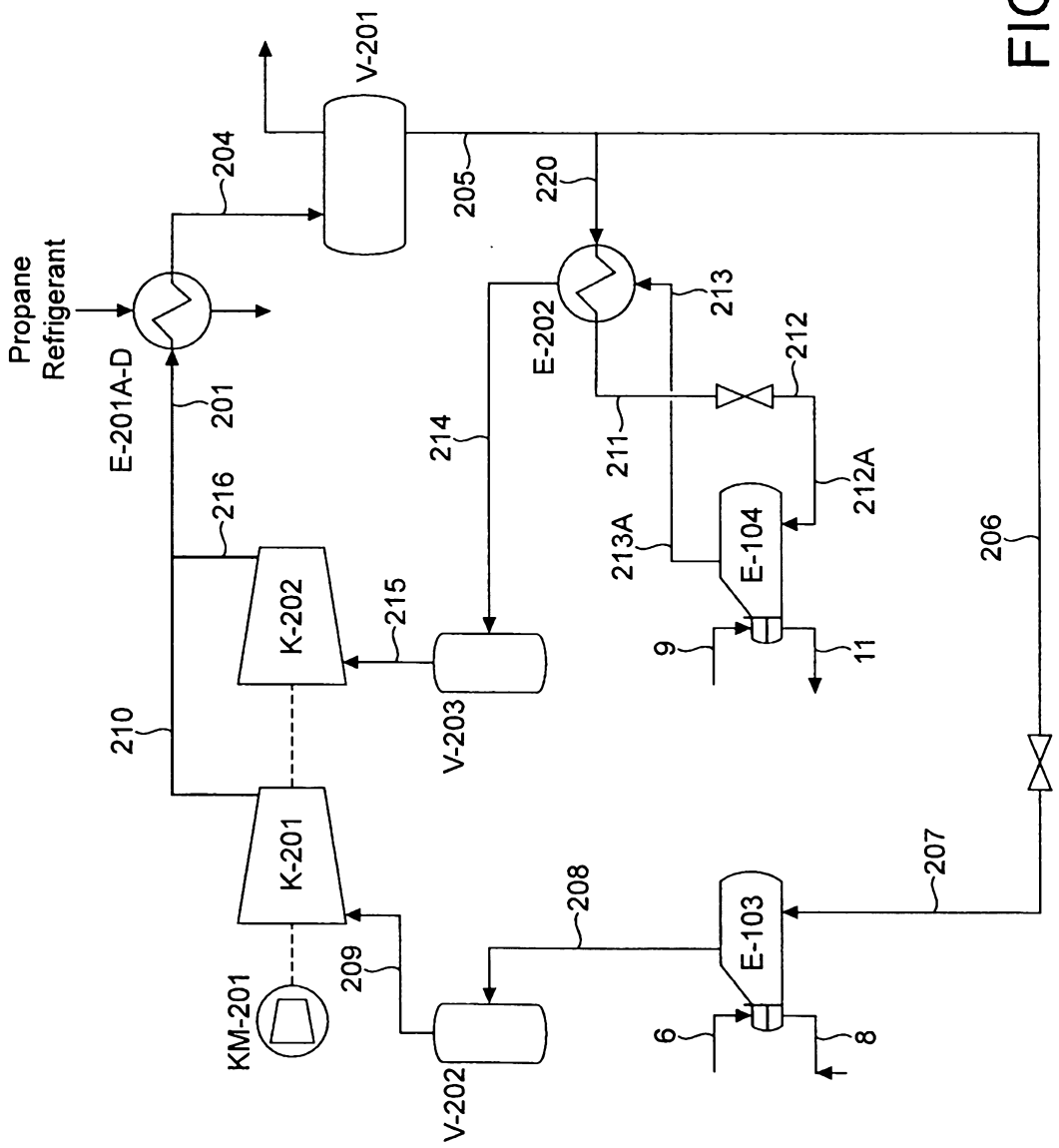
Propane
Refrigerant
E-201A-D
V-201
204
205
220
201
216
214
E-202
213
212
211
212A
213A
E-104
206
K-202
215
V-203
9
11
210
K-201
208
E-103
207
209
KM-201
V-202
6
8

FIG. 4b

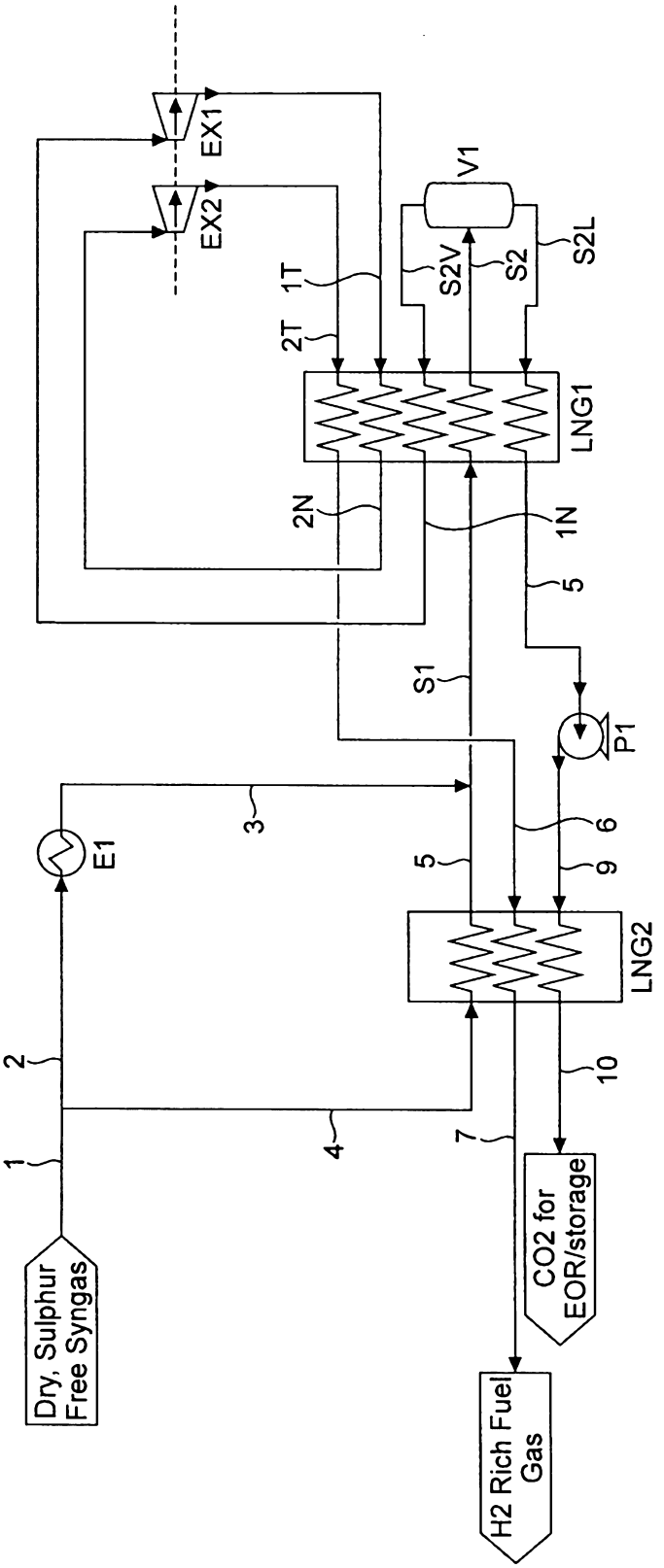
EX1
EX2
V1
S2V
S2
S2L
1T
2T
LNG1
2N
1N
5
S1
P1
3
E1
6
9
5
LNG2
2
10
1
4
7
Dry, Sulphur Free Syngas
CO2 for EOR/storage
H2 Rich Fuel Gas

FIG. 5

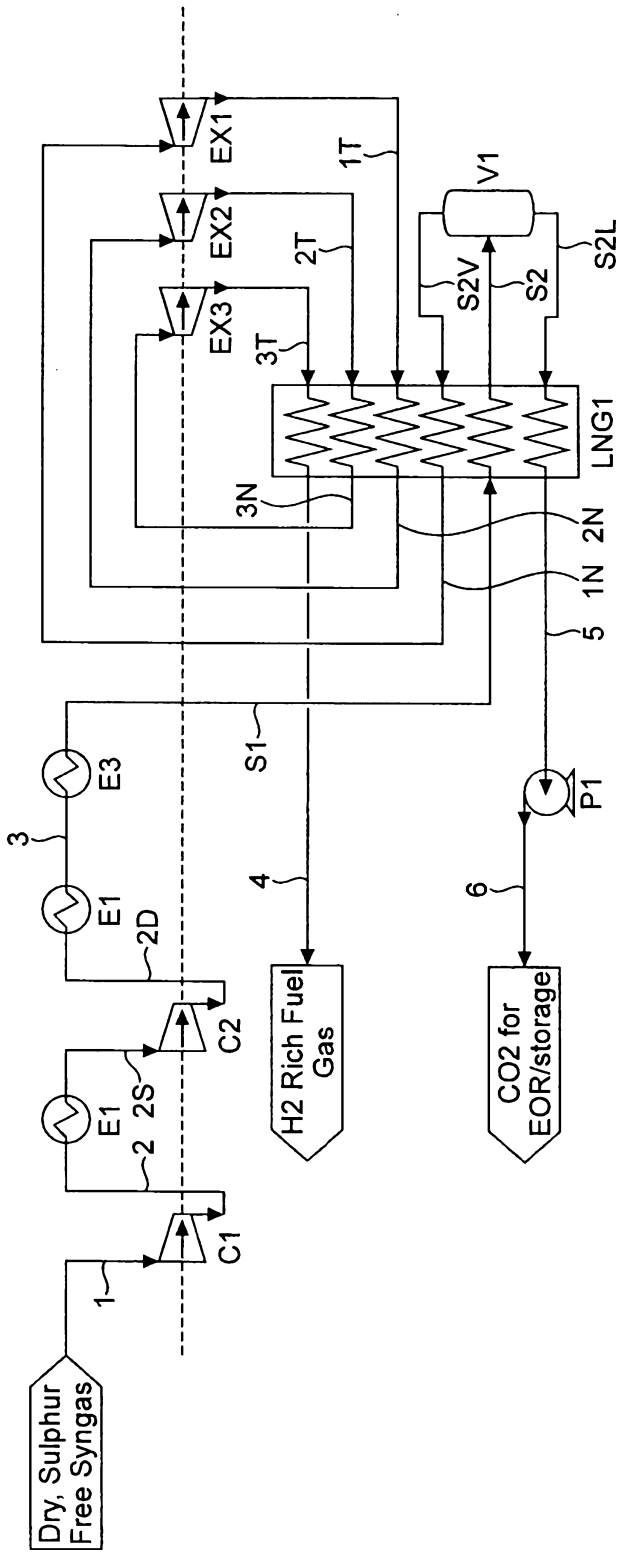
Dry, Sulphur Free Syngas
1
C1
2
E1
2S
C2
2D
E1
3
E3
4
H2 Rich Fuel Gas
S1
5
6
P1
CO2 for EOR/storage
3N
2N
1N
LNG1
3T
2T
1T
EX3
EX2
EX1
V1
S2V
S2
S2L

FIG. 6