Title: PROCESS AND APPARATUS FOR DEPLETING CARBON DIOXIDE CONTENT IN A NATURAL GAS FEED-STREAM CONTAINING ETHANE AND C3+ HYDROCARBONS

Abstract: The present invention relates to a process and apparatus for depleting carbon dioxide content in a natural gas feed-stream containing ethane and C3+ hydrocarbons to an amount at or near sales gas specification and separating the C3+ hydrocarbons therefrom. The process involves cooling the natural gas feed stream under a first set of temperature and pressure conditions arranged to produce a liquid stream of carbon dioxide, ethane and C3+ hydrocarbons and a gas stream having a reduced carbon dioxide concentration. The liquid stream is separated from the gas stream, and C3+ hydrocarbons may be separated therefrom. The gas stream is then cooled under a second set of temperature and pressure conditions arranged to produce a sweetened natural gas stream and a second liquid containing liquid carbon dioxide and/or carbon dioxide solids. The sweetened natural gas stream is separated from the second liquid. The process is particularly effective for a natural gas feedstream with a carbon dioxide content < 20% and a combined ethane and C3+ content > 5%, and is able to reduce the carbon dioxide content to < 5%.
PROCESS AND APPARATUS FOR DEPLETING CARBON DIOXIDE CONTENT
IN A NATURAL GAS FEEDSTREAM CONTAINING ETHANE AND C3+
HYDROCARBONS

Technical Field

The present invention relates to a process for depleting carbon dioxide content in a natural gas feedstream containing ethane and C3+ hydrocarbons. In particular the present invention relates to a process for depleting carbon dioxide content in a natural gas feedstream containing ethane and C3+ hydrocarbons to an amount at or near sales gas specification and separating the C3+ hydrocarbons therefrom.

Background

It is well acknowledged that it is necessary to remove sour species such as carbon dioxide or sulphur-containing compounds from natural gas prior to liquefaction or transporting by pipeline when the sour species are present at levels exceeding the allowable limit specified for a particular pipeline operation. The allowable limit of carbon dioxide content for sales gas, for example, is between 2-4%.

Several methods have been developed to separate sour species from natural gas streams including physical and chemical solvents, amine absorption systems, membrane technologies, and hybrid systems comprising a serial combination of the foregoing.

Many natural gas reserves hold feedstreams with high carbon dioxide content of up to 60% or more. While the above
separation systems can be arranged to reduce carbon dioxide content to less than 4% in the treated gas stream, the separation load placed on these systems by natural gas feedstreams rich in carbon dioxide frequently results in high capital and operational costs and development of the reserve is generally considered as economically unviable.

United States Patent No. 5,983,663 describes an alternative method for bulk removal of hydrogen sulphide and carbon dioxide only, which is particularly economical for natural gas feedstreams with H₂S and CO₂ concentrations of 10 mol% or greater and negligible quantities of ethane and higher hydrocarbons. However, the patent concedes that the process is not suitable to obtain gas streams with low H₂S and CO₂ content and if sales gas specification for H₂S and CO₂ has to be met, the process has to be augmented with a downstream Sour Gas Treating Unit (SGTU) using a physical or chemical solvent.

Selective separation of carbon dioxide from a natural gas feedstream can also be hindered by the composition of the natural gas feedstream, particularly if the natural gas feedstream is rich in ethane and C₃+ hydrocarbons. Ethane and carbon dioxide form an azeotrope while a certain proportion of C₃+ hydrocarbons have a tendency to co-condense with carbon dioxide at pressure and temperature conditions typically required to condense carbon dioxide, thus entailing a downstream separation process to separate carbon dioxide from C₃+ hydrocarbons and recover commercially valuable C₃+ hydrocarbon components. The additional separation steps increase the capital and operational costs of the natural gas processing plant.

The process in US5,983,663 does not contemplate how a gas
stream with high hydrogen sulphide and carbon dioxide content and containing ethane and higher hydrocarbons may be treated, and therefore nothing is taught in US5,983,663 about how bulk removal of sour species may be addressed in the presence of ethane and higher hydrocarbons.

Carbon dioxide can also be separated from natural gas streams to < 4% by intentionally solidifying the sour species as freezable solids, as described in International Publication Nos. WO03/062725 and WO2004/070297, or by liquefying the sour species as described in International Publication Nos. WO2004/070297 and WO2007/030888. However, it has become apparent from extensive field tests undertaken by the inventors of the present invention that the processes described therein are performed under thermodynamic factors which are limited to processing a feedstream with a carbon dioxide content of less than 15 to 25%, depending on the composition of the natural gas feedstream, to achieve a treated gas stream with a carbon dioxide content of between 2-4%.

Accordingly, a need has arisen to develop an economical process which can bulk remove sour species, such as carbon dioxide and hydrogen sulphide, from a feedstream with high carbon dioxide content of up to 60% or more containing ethane and higher hydrocarbons and to obtain a treated gas stream with a carbon dioxide content of between 2-4%.

The present invention seeks to overcome at least some of the above mentioned disadvantages.
Summary

In its broadest aspect, the invention provides a process and an apparatus for depleting the carbon dioxide content in a natural gas feedstream containing ethane and higher hydrocarbons.

Accordingly, in a first aspect, the present invention provides a process for depleting carbon dioxide content in a natural gas feedstream containing ethane and higher hydrocarbons, comprising the steps of:

(a) cooling the natural gas feedstream under a first set of temperature and pressure conditions arranged to produce a liquid stream of carbon dioxide, ethane and C3+ hydrocarbons and a gas stream having a reduced carbon dioxide concentration;

(b) separating said liquid stream from said gas stream;

(c) cooling the gas stream separated in step (b) under a second set of temperature and pressure conditions arranged to produce a sweetened natural gas stream and a second liquid containing liquid carbon dioxide and/or carbon dioxide solids; and,

(d) separating the sweetened natural gas stream from the second liquid.

In general, the natural gas feedstream has a carbon dioxide content > 20% and a combined ethane and C3+ content > 5%.

The sweetened natural gas stream resulting from the process of the present invention preferably has a carbon dioxide content of < 5% to meet sales gas specifications with negligible C3+ content.
It will be appreciated that the natural gas feedstream is dehydrated before commencing the process of the present invention.

In one embodiment of the invention, the step of cooling the natural gas feedstream comprises bringing the natural gas feedstream into contact with a heat transfer medium. In one form, bringing the natural gas feedstream in contact with a heat transfer medium includes passing the natural gas feedstream through one or more heat exchangers. The one or more heat exchangers may utilise other downstream process flows as respective coolants. In another form, bringing the natural gas feedstream in contact with a heat transfer medium includes passing the natural gas feedstream through a chiller.

In another embodiment of the invention, the step of cooling the natural gas feedstream comprises expanding the natural gas feedstream. The natural gas feedstream can be expanded through a Joule-Thomson valve, a turbo expander or a combination thereof.

In an alternative embodiment of the invention, the step of cooling the natural gas feedstream comprises bringing the natural gas feedstream in contact with a heat transfer medium as defined above followed by expanding the natural gas feedstream.

In one embodiment, the first set of temperature and pressure conditions is selected to optimise the carbon dioxide and C3+ hydrocarbon content while limiting methane content in the liquid stream to minimise methane losses in the gas stream. The first set of temperature and pressure conditions is also arranged to produce a gas stream rich in
methane with negligible C3+ hydrocarbon content to optimise C3+ hydrocarbon recovery downstream. The ethane content in the natural gas feed stream is also a factor when determining the first temperature and pressure conditions because ethane and carbon dioxide can form an azeotrope which hinders carbon dioxide separation.

In one form, the first set of temperature and pressure conditions is selected so that the liquid stream produced by the process of the present invention has greater carbon dioxide content than the gas stream.

The gas stream produced by cooling the natural gas stream under the first set of temperature and pressure conditions has a reduced carbon dioxide concentration relative to the carbon dioxide concentration of the natural gas stream. In one embodiment of the invention the concentration of carbon dioxide in the gas stream is reduced to an amount in the range of about 15 - 25%.

Advantageously, the inventors have found that a gas stream having a carbon dioxide concentration in the range of about 15 - 25% can undergo a further cooling process under cryogenic temperature and pressure conditions as described in International Publication Nos. WO03/062725, WO2004/070297, and WO2007/030888, wherein the concentration of carbon dioxide in the gas stream can be further depleted to produce sweetened natural gas with carbon dioxide content of about 2-4%.

Accordingly, in one embodiment of the invention, the second set of temperature and pressure conditions arranged to produce a sweetened natural gas stream and a second liquid
containing liquid carbon dioxide and/or carbon dioxide solids are selected to provide cryogenic conditions.

In one embodiment the step of cooling the gas stream separated in step (b) involves cooling said gas stream in a cooling vessel to an operating temperature at which carbon dioxide solids are formed or at which carbon dioxide liquefies or dissolves in a sub-cooled liquid. The step of cooling said gas stream in the cooling vessel to said temperature may comprise introducing said gas stream into said cooling vessel at a temperature that is below the operating temperature at which carbon dioxide solids are formed or at which carbon dioxide liquefies or dissolves in the sub-cooled liquid. Cooling the gas stream to a temperature at or below the operating temperature may involve expanding the gas stream as it is being fed to the cooling vessel. Alternatively, cooling the gas stream to a temperature at or below the operating temperature may involve spraying a sub-cooled liquid into the cooling vessel. In a further alternative embodiment, the gas stream may be cooled to a temperature at or below the operating temperature by both expansion and by spray-cooling. The sub-cooled liquid may be a condensate recycled from the process, including the liquid stream separated in step (b) which has been cooled, for example, by passing the liquid stream through a heat exchanger where it is cooled by indirect heat exchange with the sweetened natural gas stream.

It will be appreciated that prior to introducing said gas stream into said cooling vessel, said gas stream may be cooled to a temperature just above the operating temperature by passing said gas stream through a heat exchanger, chiller, or an expansion device. The operating temperature
is the temperature at which carbon dioxide solids will form
or the temperature at which carbon dioxide liquefies.

The term "operating temperature" is used to refer to a
temperature below the gas/solid or gas/liquid transition
temperatures for carbon dioxide at a given pressure of
operation of the cooling vessel.

If the second set of temperature and pressure conditions is
such that carbon dioxide solids (or solids of any other sour
species) are formed in the cooling vessel, the solids may be
removed from the cooling vessel in the form of a slurry, or
the solids may be first warmed to a temperature above the
operating temperature so that they melt and the subsequent
melt liquid may be removed from the cooling vessel. The
carbon dioxide solids may be warmed to a temperature above
the operating temperature by introducing a "warm" liquid
(i.e. at a temperature above the operating temperature) in
the region where the carbon dioxide solids collect.

Alternatively, the carbon dioxide solids may be warmed to a
temperature above the operating temperature by immersing a
heater in the slurry.

Optionally, subsequent to separating the sweetened natural
gas stream from the second liquid, the sweetened natural gas
stream may be contacted with a liquid solvent to facilitate
formation of a liquid solution of entrained gaseous carbon
dioxide or sour species in the liquid solvent to further
reduce the carbon dioxide content of the sweetened natural
gas. The liquid solvent comprises a solvent in which the
gaseous sour species is more soluble than in the natural gas
stream. Suitable examples of such liquid solvents comprise
any one of methanol, ethanol, dimethyl sulfoxide, ionic
liquids selected from a group comprising imidazolium,
quaternary ammonium, pyrrolidinium, pyridinium, or tetraalkylphosphonium or a NGL (natural gas liquids) condensate comprising a mixture of C2, liquefied petroleum gas components, C3, C4 and C5+ hydrocarbon components, or a combination thereof.

In a further embodiment of the invention, the process comprises separating the hydrocarbons (C3+) from the carbon dioxide and ethane in the liquid stream. The separation may be achieved by conventional techniques. It will be appreciated that the separated carbon dioxide may contain ethane, as it is likely that carbon dioxide will be separated from the C3+ hydrocarbons as a carbon dioxide-ethane azeotrope. The ethane may be separated from the carbon dioxide by passing the separated stream through a membrane or alternative conventional carbon dioxide separation means. The separated C3+ hydrocarbons may then be further separated into its distinct C3+ hydrocarbon components, including propane, butane and C5+ condensate by a downstream fractionation process.

Small amounts of liquid methane and ethane may also be produced under the first set of temperature and pressure conditions. However, it will be appreciated that entrained methane and ethane can be separated from the C3+ hydrocarbons during the aforesaid downstream fractionation, and the resulting product gas may be diverted and combined with sales gas streams.

In an alternative embodiment of the invention, prior to performing step (a), the process comprises cooling the natural gas feedstream under a third set of temperature and pressure conditions arranged to produce a C3+ hydrocarbon liquid and a C3+ hydrocarbon-depleted gas stream, and
separating the C3+ hydrocarbon liquid and the C3+ hydrocarbon-depleted gas stream. The third set of temperature and pressure conditions are selected such that the C3+ hydrocarbon liquid has negligible carbon dioxide content. The term "negligible carbon dioxide content" as used herein refers to maximum acceptable concentrations of carbon dioxide in downstream products produced by subsequent fractionation of the separated C3+ hydrocarbons. In one embodiment, the third set of temperature conditions comprise cooling the natural gas feedstream to a temperature no less than -35 °C under pressures in the range of 2,500 to 4,500 kPa.

The process may further comprise separating the C3+ hydrocarbon liquid into its C3+ hydrocarbon components, including propane, butane, and C5+ condensate, by conventional processes, such as downstream fractionation. Small amounts of liquid methane and ethane may also be produced under the third set of temperature and pressure conditions. However, it will be appreciated that entrained methane and ethane can be separated from the C3+ hydrocarbons during the aforesaid downstream fractionation, and the resulting product gas may be diverted and combined with sales gas streams, for example.

The C3+ hydrocarbon-depleted gas stream may then undergo step (a) of the process of the present invention, and so forth to deplete the natural gas stream of carbon dioxide but it will be appreciated that the liquid stream separated in step (b) will have negligible C3+ hydrocarbon content.

In a second aspect of the invention, there is provided an apparatus for depleting the carbon dioxide content in a
natural gas feedstream containing ethane and higher hydrocarbons, the apparatus comprising:

- a first cooling apparatus for cooling the natural gas feedstream under a first set temperature and pressure conditions arranged to produce a liquid stream of carbon dioxide, ethane and C3+ hydrocarbons and a gas stream having a reduced carbon dioxide concentration;

- a separator for separating said liquid stream from said gas stream; and

- a second cooling apparatus for cooling the gas stream obtained from the first separator under a second set of temperature and pressure conditions arranged to produce a sweetened natural gas stream and a second liquid containing liquid carbon dioxide and/or carbon dioxide solids.

In one embodiment, the first cooling apparatus comprises a device for bringing the natural gas feedstream and/or the gas stream produced under the first set of temperature and pressure conditions in contact with a heat transfer medium. Suitable examples of such devices include a gas-gas heat exchanger and a liquid-gas heat exchanger. Other examples of such devices include a chiller such as a refrigerated heat exchanger having one or more external refrigerants, or an absorption chiller.

In another embodiment, the first cooling apparatus comprises a gas expansion device. Suitable examples of a gas expansion device include, but are not limited to, a Joule-Thomson valve, turbo expander, and a serial combination thereof.

In an alternative embodiment, the first cooling apparatus comprises one or more heat exchangers in serial combination with a chiller. The purpose of the one or more heat...
exchangers is to reduce the cooling load on the chiller. Accordingly, the number of heat exchangers used to reduce the cooling load will be determined by the cooling load, the heat integration of available process streams within the plant to conserve energy efficiency, and the operating specifications of the heat exchangers.

It will also be appreciated that the first cooling apparatus may be a serial combination of any one or more of a heat exchanger, chiller, or a gas expansion device.

In one embodiment, the separator comprises a distillation column or a fractionating column. Preferably, the separator is a fractionating column.

The apparatus may further comprise one or more additional separators to separate hydrocarbon (C3+) components from liquid carbon dioxide in the liquid stream. Suitable examples of such separators comprise fractionators or distillation columns operating under temperature and pressure conditions to separate hydrocarbon (C3+) components such as propane, butane, and C5+ condensates.

The apparatus may further comprise one or more additional separators to separate the C3+ hydrocarbon liquid into its respective components. Suitable examples of such separators comprise fractionating or distillation columns operating under temperature and pressure conditions to separate hydrocarbon (C3+) components such as propane, butane and C5+ condensates.

In some embodiments, the first cooling apparatus and/or the second cooling apparatus cool the natural gas feedstream and/or gas stream to the extent that condensation occurs and
a mixed vapour-liquid phase fluid is produced. The apparatus of the present invention can be provided with an additional separator to separate the vapour and liquid phases and direct the vapour and liquid phases, respectively, to a fractionating column. The separator facilitates ingress of the vapour and liquid phases at appropriate regions in the fractionating column to improve the efficiency thereof. In this way, the fractionating column is arranged to fractionate the liquid stream and the gas stream to deplete the liquid bottoms of methane and enrich the top gas with methane.

In one embodiment the second cooling apparatus comprises a cooling vessel having a first inlet in fluid communication with the separator and arranged to introduce the gas stream separated from the first separator into the cooling vessel, and a first outlet for the sweetened natural gas stream and a second outlet for the second liquid. It will be appreciated that in other embodiments where a mixed vapour-liquid phase is produced in the cooling vessel, one of the first or second outlets may be configured in fluid communication with a further separator to separate the sweetened natural gas stream from the second liquid.

In one form of the invention, the first inlet may comprise an expansion device located at and/or defining the first inlet for introducing the gas stream into the cooling vessel. Suitable examples of the expansion device include a Joule-Thomson valve or a turbo expander.

It will be appreciated that the second cooling apparatus may also comprise one or more heat exchangers, chillers, and/or expansion devices to cool the gas stream to a temperature just above the operating temperature prior to introducing
the gas stream to the cooling vessel. The one or more heat exchangers, chillers, and/or expansion devices are disposed between the separator and the first inlet of the cooling vessel.

In another embodiment, the cooling vessel further comprises a second inlet for introducing a sub-cooled liquid into the cooling vessel. The second inlet is preferably located above the first inlet and comprises a plurality of spray nozzles.

Alternatively and/or additionally, the second inlet may be arranged to introduce a liquid solvent into the cooling vessel to facilitate formation of a liquid solution of entrained gaseous carbon dioxide or sour species in the liquid solvent, and thereby lower the carbon dioxide content in the sweetened natural gas stream to desired concentrations, such as for example 2-4%.

In a further embodiment, the cooling vessel may also be provided with a liquid-gas contactor to facilitate contact of the liquid solvent with the sweetened natural gas stream. Suitable examples of a liquid-gas contactor include a plurality of trays or random packing or structured packing disposed in the cooling vessel.

Description of the Figures Accompanying the Description

Preferred embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic process flow diagram depicting an apparatus in accordance with one embodiment of
the present invention for performing the process of the present invention.

**Detailed Description of the Preferred Embodiments**

Referring to Figure 1, there is shown an apparatus 10 for performing the processes of the present invention. The apparatus 10 includes a first cooling apparatus 20 for cooling a natural gas feedstream, and a fractionating column 16 for separating a liquid stream and a gas stream produced as a result of cooling the natural gas feedstream. The apparatus 10 may also include a second cooling apparatus 40 for removing remaining carbon dioxide from the natural gas feed stream under cryogenic conditions to concentrations of about 2-4%.

Prior to introduction of the dehydrated natural gas feed stream into the apparatus 10, a natural gas feed stream from a well head or storage reservoir will be subjected to a dehydration process. The resulting dehydrated natural gas feed stream typically has a water content of less than 50 ppm, and preferably less than 7 ppm. A dehydrated natural gas feed stream is particularly desirable if downstream processes operate at cryogenic temperatures in order to avoid formation of hydrates throughout the process stream.

Any suitable process for dehydrating the natural gas stream may be used. Typical examples of suitable dehydration processes include treatment of the natural gas stream with molecular sieves or dehydration using glycol or methanol. Alternatively, the natural gas stream can be dehydrated by formation of methane hydrates: for example, such as by using a dehydration process described in WO 2004/070297. In the particular embodiment shown in Figure 1, the natural gas
feed stream is dehydrated by passing it through molecular sieves 12. A particulate filter may be provided subsequent to the molecules sieves 12 to ensure solids do not enter downstream operations.

The preferred input pressure for the dehydrated natural gas feed stream is in the range of 5500 to 7000 kPa to optimise component separations and energy efficiency within the apparatus 10. As shown in Figure 1, if the input pressure is less than desired, the dehydrated natural gas feed stream is preferably compressed via compressor 14 to a pressure in the range 5500 to 7000 kPa. It will be appreciated that if the input pressure is greater than desired, the dehydrated natural gas feed stream may be expanded to reduce the pressure thereof to a pressure in the range of 5,500 to 7,000 kPa. Advantageously, expansion of said feed stream will cool it, thereby reducing the cooling load. The dehydrated natural gas feed stream is then fed to the first cooling apparatus 20 via conduit 102 at a temperature in the range of 40 to 60°C.

Referring to Figure 1, the first cooling apparatus 20 comprises a heat exchanger train including a first heat exchanger 22, a second heat exchanger 24, and a third heat exchanger 26 configured in serial combination with a chiller 28. Suitable examples of heat exchangers include gas-gas heat exchangers and gas-liquid heat exchangers. In this particular embodiment, the chiller 28 is a refrigerated heat exchanger chilled by a first refrigerant, such as for example propane or ammonia. The first refrigerant is provided from a first refrigeration circuit 50.

The purpose of the first, second, and third heat exchangers 22, 24, 26 is to reduce the cooling load on the chiller 28.
It will be appreciated that further heat exchangers could be configured in serial combination with the first, second, and third heat exchangers 22, 24, 26 to further reduce the cooling load on the chiller 28. Conversely, any one or more of the first, second, and third heat exchangers 22, 24, 26 could be omitted from the first cooling apparatus 20 if the cooling load demands on the chiller 28 were lower.

For the purposes of energy conservation within the apparatus 10, it is preferable that the first, second, and third heat exchangers 22, 24, 26 utilise downstream process flows produced in other parts of the apparatus 10 as cooling media to cool the compressed dehydrated natural gas feedstream. For example, in the particular embodiment shown in Figure 1 the first heat exchanger 22 uses liquid carbon dioxide as the coolant therefor; the second heat exchanger 24 uses a sweetened natural gas as the coolant therefor; and the third heat exchanger 26 uses the liquid stream arising from the separator 30 as the coolant therefor.

Accordingly, in the particular embodiment shown in Figure 1, the compressed dehydrated natural gas feedstream is directed via conduit 102 to the first heat exchanger 22 where it is cooled to a temperature in the range of 50°C to 0°C. Said feedstream is then directed via conduit 201 to the second heat exchanger 24 where it is cooled to a temperature in the range of 0 to -5°C, whereafter said feedstream is directed via conduit 202 to the third heat exchanger 26 were it is cooled to a temperature in the range of -5 to -15°C. Preferably, the one or more heat exchangers cool the feedstream to at least -15°C.

The cooled feedstream is then directed to the chiller 28 where it is cooled to a temperature in the range of -15 to -
Some cooled feedstream is condensed in the chiller 28. The resulting liquid and vapour phases are separated in separator 30, then fed to fractionating column 16.

Optionally, as envisaged in this particular embodiment, the liquid phase may be diverted through conduit 207 to the third heat exchanger 26 via Joule-Thomson valve 18, then recirculated to the fractionating column 16 via conduit 209.

The fractionating column 16 receives the liquid and vapour phases on individual trays corresponding to their respective temperatures and approximate compositions. Typically, the liquid phase comprises liquid carbon dioxide, ethane and hydrocarbons (C3+). However, in some embodiments of the invention wherein the liquid phase also comprises liquid methane, fractionating the liquid phase and the gas phase in the fractionating column 16 depletes the resulting liquid stream of methane and enriches the resulting gas stream with methane.

The fractionating column 16 is operated under a first set of temperature and pressure conditions arranged to produce a gas stream with a carbon dioxide content less than the predetermined carbon dioxide concentration, and a liquid stream containing liquid carbon dioxide, ethane and C3+ hydrocarbons. Preferably, the predetermined concentration of carbon dioxide in the gas stream is an upper limit of carbon dioxide concentration in the gas stream at which a subsequent sweetening process for removal of carbon dioxide from the gas stream can effectively operate in the second cooling apparatus 40. Preferably, the upper limit of carbon dioxide concentration in the gas stream is in the range of 20 to 25%. However, it will be understood that the first
set of temperature and pressure conditions can be arranged to provide a gas stream with a carbon dioxide content < 20%.

Typically, the first set of temperature and pressure conditions are also arranged to produce a gas stream rich in methane with negligible C3+ hydrocarbon content to optimise C3+ hydrocarbon recovery downstream, and a liquid stream with negligible methane content to minimise methane losses.

It will be appreciated that both the gas stream and the liquid stream are likely to contain ethane in variable proportions depending on the original composition of the natural gas feed stream and the first set of temperature and pressure conditions under which the natural gas feed stream is cooled.

Typically, the vapour stream is removed from the fractionating column 16 at temperatures in the range of -20 to -35°C, and the liquid stream is removed from the fractionating column 16 at temperatures in the range of 15 to 25°C.

In some embodiments of the invention, the process further comprises separating the C3+ hydrocarbons from liquid carbon dioxide in the liquid stream. The liquid stream is directed via conduit 220 to a C3+ hydrocarbon fractionation train 70 to separate propane, butane and condensate from the ethane and carbon dioxide components in the liquid stream.

The C3+ hydrocarbon fractionation train 70 includes a first fractionation column 72, a second fractionation column 74, and a third fractionation column 76. The first fractionation column 72 is operated to limit ethane and carbon dioxide content in a first bottoms stream, and to
limit propane content in a first overhead stream to maximize propane product. The first overhead stream is rich in carbon dioxide and is typically condensed in readiness for sequestration. Alternatively, the first overhead stream may be processed in a membrane system or other suitable means (not shown) to separate ethane and carbon dioxide in order to recover ethane for sales, and produce a carbon dioxide rich stream. Subsequently, the carbon dioxide rich stream may be compressed, cooled, and combined with liquid carbon dioxide produced in the second cooling apparatus 40 as will be described later, for sequestration purposes.

The first bottoms stream is directed to the second fractionation column 14 via conduit 303 for separation into a second overhead stream comprising propane and a second bottoms stream. The second bottoms stream is subsequently directed to the third fractionation column 16 via conduit 304 for separation into a third overhead stream comprising butane and a third bottoms stream comprising condensate.

The gas stream produced in the fractionating column 16 is rich in methane but still contains carbon dioxide in concentrations greater than typical sales gas specifications; for example, 15 to 20%. Accordingly, the gas stream must undergo further processing to substantially deplete carbon dioxide in the gas stream to desirable concentrations. In this particular embodiment as described with reference to Figure 1, the gas stream is treated at cryogenic temperatures in the second cooling apparatus 40 to produce carbon dioxide solids and thereby remove the freezable solid species by gravity separation and produce a sweetened natural gas stream.
The second cooling apparatus 40 includes a heat exchange train 42 to cool the gas stream to just above the carbon dioxide solid formation temperature, and a cooling vessel 44 in which the gas stream is cooled to a temperature where carbon dioxide solids form. The heat exchange train 42 in this particular embodiment comprises a first heat exchanger 41, a second heat exchanger 43, and a third heat exchanger 45.

For the purposes of energy conservation within the apparatus 10, it is preferable that the first, second, and third heat exchangers 41, 43, 45, utilise downstream process flows produced in other parts of the apparatus 10 as cooling media to cool the compressed dehydrated natural gas feedstream, where possible. For example, in the particular embodiment shown in Figure 1 the first heat exchanger 41 is disposed in a lower portion of the cooling vessel 44 and is configured to operate as an immersion heater. Thermal energy from the gas stream is utilised to liquefy carbon dioxide solids which have collected in the lower portion of the cooling vessel 44 before removal from the cooling vessel 44 as liquid carbon dioxide. Alternatively, the gas stream is cooled before passing to the second heat exchanger 43. The second heat exchanger 43 uses sweetened natural gas produced in the cooling vessel 44 as the coolant therefor; and the third heat exchanger 43 is a refrigerated heat exchanger which uses a second refrigerant, such as ethylene, from a second refrigeration unit 60.

The cooled gas stream is then fed to the cooling vessel 44 via conduit 213. Typically, the cooled gas stream is cooled to a temperature at or below the temperature at which carbon dioxide solids or liquids form by expanding the cooled gas stream using a Joule-Thomson valve 46 or other suitable gas
expander such as a turbo expander to further cool the stream as it enters the vessel 44. In one embodiment, the cooled gas stream is expanded using a turbo expander in sequential combination with the Joule-Thomson valve 46. In this particular embodiment, the Joule-Thomson valve 46 defines the input port of the cooling vessel 44.

Expanding the cooled gas stream upon introduction to the cooling vessel 44 achieves a second set of temperature and pressure conditions within the cooling vessel 44 at which the carbon dioxide species contained in the cooled gas stream solidify or liquefy, resulting in the production of a sweetened natural gas stream. Typically, the temperature and pressure conditions within the cooling vessel 44 are in the range of -70 to -160°C and 15 to 30 bar.

The sweetened natural gas stream is removed from the cooling vessel 44 via conduit 215 and directed through the second heat exchangers 24, 43, and then discharged from the apparatus 10 to sales.

A small amount of liquid condensate of hydrocarbons will typically also form under the temperature and pressure conditions in the cooling vessel 44. Under conditions where carbon dioxide solids form, the solids and the liquid condensate migrate to the lower portion of the cooling vessel 44 under gravity separation, thereby forming a slurry of natural gas liquids and carbon dioxide solids. In other embodiments, separation of the slurry from the resulting sweetened natural gas stream may be achieved or enhanced by the use of centrifugal force or inlet devices configured to coalesce liquid droplets or agglomerate solid particles. Alternatively, a mixture of liquid carbon dioxide, other
sour species and liquid condensate accumulates in a lower portion of the cooling vessel 44 under gravity.

The slurry of solid carbon dioxide particles can then be heated to a temperature at least marginally greater than the solidification temperature to melt the solid carbon dioxide particles in the lower portion of the cooling vessel 44. The nature and concentration of carbon dioxide in the resultant second liquid is highly dependant on the composition of the cooled gas stream treated in the cooling vessel 44. For example, concentrations of carbon dioxide in the second liquid can be >90%. In this embodiment the cooling vessel 44 is provided with an immersion heater (not shown) which heats the slurry up to a temperature at least marginally greater than the carbon dioxide melting point temperature. In this embodiment, as described previously, the immersion heater is the first heat exchanger 41 which uses the vapour phase generated in the fractionating column 16 and diverted through conduit 210 to transfer its thermal energy to raise the temperature in the lower portion of the cooling vessel 44. In small volume applications, the immersion heater may be powered by electricity. Alternatively, a liquid process stream derived from another part of the process plant and at a higher temperature than the melting point temperature of carbon dioxide can be introduced into the lower portion of the cooling vessel 44 and mixed with the slurry to melt the carbon dioxide solids.

The second liquid is removed from the cooling vessel 44 through conduit 217 and directed to a carbon dioxide pump feed drum 47 where it is combined with the first overhead stream of the first fractionation column 72 and discharged, preferably for sequestration. The combined liquid carbon
dioxide stream can be used as a coolant in heat exchangers to conserve thermal energy in the apparatus 10.

In an alternative configuration (not shown) the fractionating column 16 is operated under a third set of temperature and pressure conditions arranged to produce a gas stream with methane, ethane and carbon dioxide, and a liquid stream containing C3+ hydrocarbons.

The C3+ hydrocarbon liquid may be diverted to second fractionation column 74 and third fractionation column 76 to separate the C3+ hydrocarbon liquid into its propane, butane, and C5+ condensate components respectively.

The gas stream from fractionating column 16 may be diverted to first fractionation column 72 where, under the first set of temperature and pressure conditions, a liquid stream of carbon dioxide, and a gas stream having a reduced carbon dioxide concentration of about 15-25% is produced. Said gas stream is fed to the second cooling apparatus 40 where it is treated under the second set of temperature and pressure conditions as described above to deplete the remaining carbon dioxide content of the gas to about 2-4%. The liquid stream of carbon dioxide may be directed to sequestration or combined with other liquid streams of carbon dioxide produced in other parts of the apparatus 10, such as for example, the second cooling apparatus 40.

Example

A 60 MMSCFD natural gas feedstream with composition as defined in Table 1 at 20 °C and 4450 kPa was dehydrated by passing the natural gas feedstream over a molecular sieves package. The dehydrated natural gas feedstream was
compressed to 6300 kPa, the temperature of the compressed dehydrated natural gas feedstream consequently rising to 50°C. Said feedstream was progressively cooled to 0°C in a first heat exchanger, -5°C in a second heat exchanger, and -13°C in a third heat exchanger. The cooled feedstream was then chilled to -18°C in a refrigerated heat exchanger then fed to a separator to separate the resultant liquid and vapour phases.

The liquid and vapour phases were recombined and fractionated in a fractionation column at 5550 kPa to produce a liquid stream containing C3+ hydrocarbons and carbon dioxide at a concentration less than 25%, and a vapour stream. The liquid stream was separated at a temperature of 23°C and the vapour stream was separated at a temperature of -34°C.

The liquid stream was directed to a series of fractionation columns to separate propane, butane and condensate streams from a carbon dioxide stream.

The aforementioned vapour stream was further cooled to -37°C in a first heat exchanger, -44°C in a second heat exchanger, and then to -70°C in a third heat exchanger. The cooled vapour stream was then expanded through a Joule-Thomson valve into a cooling vessel from 5380 kPa to 1655 kPa which cooled aforesaid vapour stream to -85°C, thereby forming a slurry of carbon dioxide solids and liquid methane condensate, and a sweetened natural gas stream appropriate for sales. The solids in the slurry were melted, and the liquid carbon dioxide stream was diverted for sequestration.

The recoveries of the components of the feedstream are provided in Tables 2 and 3, and the specification of each
product stream derived from the above process is provided in Table 4.

Table 1: Natural gas feedstream composition

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<tr>
<th>Component</th>
<th>Mol %</th>
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<tr>
<td>Methane</td>
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<td>Ethane</td>
<td>5.46</td>
</tr>
<tr>
<td>Propane</td>
<td>3.31</td>
</tr>
<tr>
<td>Iso-butane</td>
<td>0.85</td>
</tr>
<tr>
<td>n-butane</td>
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<tr>
<td>Neo-pentane</td>
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<td>0.22</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.16</td>
</tr>
<tr>
<td>Hexanes</td>
<td>0.12</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>43.70</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.29</td>
</tr>
<tr>
<td>Heptanes</td>
<td>0.10</td>
</tr>
<tr>
<td>Octanes</td>
<td>0.07</td>
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<td>100.00</td>
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Table 2: Recoveries of feed components into various product streams on a mass basis

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed (60mmscfd) (kg/h)</th>
<th>Sales Gas (kg/h)</th>
<th>Propane Product (kg/h)</th>
<th>Butane Product (kg/h)</th>
<th>Condensate Product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>21,748</td>
<td>21,199</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ethane</td>
<td>4,893</td>
<td>2,018</td>
<td>10</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Propane</td>
<td>4,227</td>
<td>102</td>
<td>3,094</td>
<td>74</td>
<td>0</td>
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<tr>
<td>Butane</td>
<td>2,619</td>
<td>0</td>
<td>456</td>
<td>2,105</td>
<td>37</td>
</tr>
<tr>
<td>C5+</td>
<td>1,490</td>
<td>0</td>
<td>9</td>
<td>56</td>
<td>1,425</td>
</tr>
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</table>
Table 3: Recoveries of each of the feed components into individual product streams on percentage basis

<table>
<thead>
<tr>
<th>Component</th>
<th>Gas (%)</th>
<th>Propane Product (%)</th>
<th>Butane Product (%)</th>
<th>Condensate Product (%)</th>
<th>Total Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>97.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>97.5</td>
</tr>
<tr>
<td>Ethane</td>
<td>41.2</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>41.4</td>
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<tr>
<td>Propane</td>
<td>2.4</td>
<td>73.2</td>
<td>1.8</td>
<td>0.0</td>
<td>77.4</td>
</tr>
<tr>
<td>Butane</td>
<td>0.0</td>
<td>17.4</td>
<td>80.4</td>
<td>1.4</td>
<td>99.2</td>
</tr>
<tr>
<td>C5+</td>
<td>0.0</td>
<td>0.6</td>
<td>3.8</td>
<td>95.6</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 4: Specifications for each product stream

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed (60mmscfd)</th>
<th>Sales Gas</th>
<th>Propane Product</th>
<th>Butane Product</th>
<th>Condensate Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (mol%)</td>
<td>45.4</td>
<td>89.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethane (mol%)</td>
<td>5.4</td>
<td>4.5</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Propane (mol%)</td>
<td>3.2</td>
<td>0.2</td>
<td>89.4</td>
<td>4.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Butane (mol%)</td>
<td>1.5</td>
<td>0.1</td>
<td>9.9</td>
<td>93.5</td>
<td>3.6</td>
</tr>
<tr>
<td>C5+ (mol%)</td>
<td>1.00</td>
<td>0.0</td>
<td>0.1</td>
<td>2.2</td>
<td>96.4</td>
</tr>
<tr>
<td>Nitrogen (mol%)</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Carbon Dioxide (mol%)</td>
<td>43.5</td>
<td>4.9</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Wobbe Index</td>
<td>N/A</td>
<td>46.75</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Vapour Pressure @37.8C (kPag)</td>
<td>N/A</td>
<td>N/A</td>
<td>1126</td>
<td>356</td>
<td>-11</td>
</tr>
</tbody>
</table>
The Claims Defining the Invention are as follows:

1. A process for depleting carbon dioxide content in a natural gas feedstream containing ethane and higher hydrocarbons, comprising the steps of:
   (a) cooling the natural gas feedstream under a first set of temperature and pressure conditions arranged to produce a liquid stream of carbon dioxide, ethane and C3+ hydrocarbons and a gas stream having a reduced carbon dioxide concentration;
   (b) separating said liquid stream from said gas stream;
   (c) cooling the gas stream separated in step (b) under a second set of temperature and pressure conditions arranged to produce a sweetened natural gas stream and a second liquid containing liquid carbon dioxide and/or carbon dioxide solids; and,
   (d) separating the sweetened natural gas stream from the second liquid.

2. The process according to claim 1, where the natural gas feedstream has a carbon dioxide content > 20% and a combined ethane and C3+ content > 5%.

3. The process according to claim 1 or claim 2, wherein the sweetened natural gas stream has a carbon dioxide content of < 5%.

4. The process according to any one of the preceding claims, wherein the natural gas feedstream is dehydrated before commencing step (a).

5. The process according to any one of the preceding claims, wherein the step of cooling the natural gas...
feedstream comprises bringing the natural gas feedstream into contact with a heat transfer medium.

6. The process according to claim 5, wherein bringing the natural gas feedstream in contact with a heat transfer medium comprises passing the natural gas feedstream through one or more heat exchangers.

7. The process according to claim 5, wherein bringing the natural gas feedstream in contact with a heat transfer medium includes passing the natural gas feedstream through a chiller.

8. The process according to any one of claims 1 to 4, wherein the step of cooling the natural gas feedstream comprises expanding the natural gas feedstream.

9. The process according to any one of the preceding claims, wherein the step of cooling the natural gas feedstream comprises bringing the natural gas feedstream in contact with a heat transfer medium as defined in any one of claims 5 to 7 followed by expanding the natural gas feedstream.

10. The process according to any one of the preceding claims, wherein the first set of temperature and pressure conditions is selected to optimise the carbon dioxide and C3+ hydrocarbon content while limiting methane content in the liquid stream.

11. The process according to any one of the preceding claims, wherein the first set of temperature and pressure conditions is arranged to produce a gas stream rich in methane with negligible C3+ hydrocarbon content.
12. The process according to any one of the preceding claims, wherein the first set of temperature and pressure conditions is selected so that the liquid stream has greater carbon dioxide content than the gas stream.

13. The process according to any one of the preceding claims, wherein the concentration of carbon dioxide in the gas stream is reduced to an amount in the range of about 15 - 25 %.

14. The process according to any one of the preceding claims, wherein the step of cooling the gas stream separated in step (b) under a second set of temperature and pressure conditions comprises cooling said gas stream in a cooling vessel to an operating temperature at which carbon dioxide solids are formed or at which carbon dioxide liquefies or dissolves in a sub-cooled liquid.

15. The process according to claim 14, wherein the step of cooling said gas stream in the cooling vessel to said operating temperature may comprise introducing said gas stream into said cooling vessel at a temperature that is below the operating temperature.

16. The process according to claim 14 or claim 15, wherein cooling the gas stream to a temperature at or below the operating temperature may involve expanding the gas stream as it is being introduced to the cooling vessel.

17. The process according to claim 14 or claim 15, wherein cooling the gas stream to a temperature at or below the operating temperature may involve spraying a sub-cooled liquid into the cooling vessel.
18. The process according to claim 16 or claim 17, wherein the gas stream is cooled to a temperature at or below the operating temperature by both expansion and by spray-cooling.

19. The process according to any one of claims 14 to 18, wherein prior to introducing said gas stream into said cooling vessel, said gas stream is cooled to a temperature at or just above the operating temperature.

20. The process according to any one of claims 14 to 19, wherein the solids are removed from the cooling vessel in the form of a slurry, or the solids are first warmed to a temperature above the operating temperature so that they melt and the subsequent melt liquid is removed from the cooling vessel.

21. The process according to claim 20, wherein the carbon dioxide solids are warmed to a temperature above the operating temperature by introducing a liquid at a temperature above the operating temperature in a region of the cooling vessel where the carbon dioxide solids collect.

22. The process according to claim 20, wherein the carbon dioxide solids are warmed to a temperature above the operating temperature by immersing a heater in the slurry.

23. The process according to any one of claims 14 to 19, wherein the operating temperature is a temperature at which liquid carbon dioxide forms.

24. The process according to any one of the preceding claims, wherein prior to separating the sweetened natural
gas stream from the second liquid, the sweetened natural gas stream is contacted with a liquid solvent to facilitate formation of a liquid solution of entrained gaseous carbon dioxide or sour species in the liquid solvent.

25. The process according to claim 24, wherein the liquid solvent comprises a solvent in which the gaseous sour species is more soluble than in the natural gas stream.

26. The process according to any one of the preceding claims, wherein the process further comprises separating the hydrocarbons (C3+) from the carbon dioxide in the liquid stream.

27. The process according to claim 26, wherein the separated C3+ hydrocarbons are then further separated into distinct C3+ hydrocarbon components, including propane, butane and C5+ condensate.

28. The process according to any one of claims 1 to 25, wherein prior to performing step (a), the process comprises cooling the natural gas feedstream under a third set of temperature and pressure conditions arranged to produce a C3+ hydrocarbon liquid and a C3+ hydrocarbon-depleted gas stream, and separating the C3+ hydrocarbon liquid and the C3+ hydrocarbon-depleted gas stream.

29. The process according to claim 28, wherein the third set of temperature and pressure conditions is selected such that the C3+ hydrocarbon liquid has negligible carbon dioxide content.

30. The process according to claim 28 or claim 29, wherein the third set of temperature conditions comprise cooling the
natural gas feedstream to a temperature no less than -35 °C under pressures in the range of 2,500 to 4,500 kPa.

31. An apparatus for depleting the carbon dioxide content in a natural gas feedstream containing ethane and higher hydrocarbons, the apparatus comprising:

a first cooling apparatus for cooling the natural gas feedstream under a first set temperature and pressure conditions arranged to produce a liquid stream of carbon dioxide, ethane and C3+ hydrocarbons and a gas stream having a reduced carbon dioxide concentration;

a separator for separating said liquid stream from said gas stream; and

a second cooling apparatus for cooling the gas stream obtained from the first separator under a second set of temperature and pressure conditions arranged to produce a sweetened natural gas stream and a second liquid containing liquid carbon dioxide and/or carbon dioxide solids.

32. The apparatus according to claim 31, wherein the first cooling apparatus comprises a device for bringing the natural gas feedstream and/or the gas stream produced under the first set of temperature and pressure conditions in contact with a heat transfer medium.

33. The apparatus according to claim 32, wherein the device comprises a gas-gas heat exchanger, liquid-gas heat exchanger, or a chiller.

34. The apparatus according to claim 31, wherein the first cooling apparatus comprises a gas expansion device.
35. The apparatus according to claim 33, wherein the gas expansion device comprises a Joule-Thomson valve, turbo expander, and a serial combination thereof.

36. The apparatus according to claim 31, wherein the first cooling apparatus comprises a serial combination of any one or more of a heat exchanger, chiller, or a gas expansion device.

37. The apparatus according to any one of claims 31 to 36, wherein the separator comprises a distillation column or a fractionating column.

38. The apparatus according to claim 37, further comprising one or more additional separators to separate hydrocarbon (C3+) components from liquid carbon dioxide in the liquid stream.

39. The apparatus according to claim 38, further comprising one or more additional separators to separate the C3+ hydrocarbon liquid into its respective components.

40. The apparatus according to any one of claims 31 to 39, wherein the second cooling apparatus comprises a cooling vessel having a first inlet in fluid communication with the separator and arranged to introduce the gas stream separated from the first separator into the cooling vessel, and a first outlet for the sweetened natural gas stream and a second outlet for the second liquid.

41. The apparatus according to claim 40, wherein the first inlet comprises an expansion device located at and/or defining the first inlet for introducing the gas stream into the cooling vessel.
42. The apparatus according to claim 40 or claim 41, wherein the second cooling apparatus further comprises one or more heat exchangers, chillers, and/or expansion devices to cool the gas stream to a temperature just above the operating temperature prior to introducing the gas stream to the cooling vessel.

43. The apparatus according to claim 42, wherein the one or more heat exchangers, chillers, and/or expansion devices are disposed between the separator and the first inlet of the cooling vessel.

44. The apparatus according to any one of claims 40 to 43, wherein the cooling vessel further comprises a second inlet for introducing a sub-cooled liquid into the cooling vessel.

45. The apparatus according to claim 44, wherein the second inlet is preferably located above the first inlet and comprises a plurality of spray nozzles.

46. The apparatus according to claim 44 or claim 45, wherein the second inlet is alternatively and/or additionally arranged to introduce a liquid solvent into the cooling vessel to facilitate formation of a liquid solution of entrained gaseous carbon dioxide or sour species in the liquid solvent, and thereby lower the carbon dioxide content in the sweetened natural gas stream.

47. The apparatus according to any one of claims 40 to 46, wherein the cooling vessel may also be provided with a liquid-gas contactor to facilitate contact of the liquid solvent with the sweetened natural gas stream.
48. The apparatus according to claim 47, wherein the liquid-gas contactor comprises a plurality of trays or random packing or structured packing disposed in the cooling vessel.
**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl.

C10G 5/06 (2006.01)  F25J 3/00 (2006.01)  F25J 3/08 (2006.01)
C10L 3/10 (2006.01)  F25J 3/02 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

REFER ELECTRONIC DATA BASE CONSULTED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI IPC C10G 5/06, C10L 3/10, F25J 3/00, 3/02, 3/08 & Keywords (liquefied gas + or cool+ or solid+ and dioxid+ and (town gas) or LNG or (natural gas))

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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[ ] Further documents are listed in the continuation of Box C

[ ] See patent family annex

* Special categories of cited documents

  'A' document defining the general state of the art which is not considered to be of particular relevance

  'E' earlier application or patent but published on or after the international filing date

  'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

  'O' document referring to an oral disclosure, use, exhibition or other means

  'P' document published prior to the international filing date but later than the priority date claimed

  'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

  'X' document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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  '&document member of the same patent family

Date of the actual completion of the international search: 02 April 2008

Date of mailing of the international search report: 09 APR 2008

Authorized officer

ASOKA DIAS-ABEYGAWARDENA

AUSTRALIAN PATENT OFFICE

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Telephone No: (02) 6283 2141
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX