(57) Abrégé/Abstract:
A process for removal of sour species from a dehydrated natural gas feed stream is provided. The dehydrated natural gas feed stream is cooled to conditions where a slurry of solid sour species and hydrocarbon liquids is formed together with a gaseous stream containing gaseous sour species. The gaseous stream containing gaseous sour species is then separated from the slurry and treated with a liquid solvent, thereby forming a liquid solution of the sour species and a dehydrated sweetened natural gas product stream. An apparatus for removing sour species from a dehydrated natural gas feed stream is also provided. The apparatus has a vessel with a solids formation zone in fluid communication with a gas solvation zone. The solids formation zone is configured to facilitate formation of a slurry of solid sour species and hydrocarbon liquids and a gaseous stream containing gaseous sour species. The gas solvation zone is configured to facilitate formation of a liquid solution of sour species. The apparatus has an inlet for introducing the dehydrated natural gas feed stream to the solids formation zone, a conduit configured to direct the gaseous stream from the solids formation zone to the gas solvation zone, and an inlet for introducing liquid solvent into the gas solvation zone.
PROCESS AND APPARATUS FOR REMOVAL OF SOUR SPECIES FROM A NATURAL GAS STREAM

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PROCESS AND APPARATUS FOR REMOVAL OF SOUR SPECIES FROM A
NATURAL GAS STREAM

Field of the Invention

The present invention relates to a process and apparatus for removal of sour species from a natural gas stream. In particular, the present invention relates to a process for removal of sour species in a liquid phase from a dehydrated natural gas stream.

The present invention also relates to a process for recovering liquid carbon dioxide from a natural gas stream.

Background of the Invention

Natural gas from either production reservoirs or storage reservoirs typically contains water, as well as other species, which form solids in low temperature conditions under which some process operations are performed.

The formation of solids in pipe work, on the surface of heat exchangers and/or liquefaction and storage vessels is undesirable, as the accumulation of such solids eventually results in decreased operating and storage efficiencies, damage, and increased plant down time for maintenance and repair.

Furthermore, several species, in particular carbon dioxide (CO₂), hydrogen sulphide (H₂S), mercaptans, and mercury which
are also referred to as "sour" species, promote corrosion within gas pipework. Additionally, in some jurisdictions, it may be necessary to comply with legal or commercial requirements concerning minimum concentrations of sour species within a natural gas product stream.

Several sorption methods have been developed to dehydrate a feed gas from a wellhead or a storage reservoir and then treat the dehydrated gas stream to remove or deplete the sour species contained therein. The most extensively used methods rely on the use of various types of molecular sieves and physical and chemical absorption systems. It is generally acknowledged that these methods, while effective, are complex and expensive to implement, particularly in respect to large volume plants, and operational problems are frequently encountered.

More recently, there has been considerable focus on methods for separating water or sour species from the natural gas stream by intentionally solidifying the water as hydrates and/or the sour species as freezable solids.

The solid forming property of carbon dioxide and the low vapour phase solubility of carbon dioxide at cold temperatures form the basis for the separation process described in US 5,819,555. A cooled feed stream of natural gas enters a separation vessel where process means are provided to produce and separate carbon dioxide solids. Carbon dioxide is removed from the vessel as a carbon dioxide rich liquid stream, while purified cold vapour is removed from the separation vessel as
a product stream.

International Publication No. WO 03/062725 describes a process for the removal of freezable species such as carbon dioxide, water and heavy hydrocarbons from a natural gas feed stream during liquefaction to produce liquid natural gas (LNG). The freezable species are removed as a LNG slurry of the freezable species.

The process described in International Publication No. WO 2004/070297 is represented as an improvement on the process and device discussed in International Publication No. WO 03/062725. The natural gas feed stream is cooled in a first vessel to a first operating temperature at which hydrates are formed, and the resulting stream of dehydrated gas is then cooled in a second vessel to a second operating temperature at which solids of the sour species are formed or at which the sour species dissolve in a liquid. A stream of dehydrated sweetened gas is removed from the second vessel.

In practice the process described in WO 2004/070297 involves spray cooling of the dehydrated gas in the second vessel with a sub-cooled liquid comprising a condensate of the dehydrated gas containing sour species produced in the first vessel, in order to effect enhanced cooling within the second vessel. However, an unfortunate side effect of using said sub-cooled liquid is that the heavier hydrocarbons contained in the liquid are removed with the sour species making recovery of the hydrocarbons difficult or costly to achieve.
The present invention seeks to overcome at least some of the aforementioned disadvantages.

It is to be understood that, although prior art use and publications may be referred to herein, such reference does not constitute an admission that any of these form a part of the common general knowledge in the art, in Australia or any other country.

Summary of the Invention

It has been demonstrated that a dehydrated natural gas stream may be sweetened by solidifying sour species contained therein. However, at any fixed temperature, the solid sour species has a characteristic fixed vapour pressure, and thus sour species will also be present in the vapour phase. The present invention is based on the realisation that it is possible to sequentially and selectively separate solid, liquid and gaseous fractions of a contaminant sour species from a dehydrated natural gas feed stream, thereby enhancing the removal of sour species from the dehydrated natural gas product stream.

Thus, the present invention provides a process for removing a sour species from a dehydrated natural gas feed stream comprising the steps of:

a) cooling the dehydrated natural gas feed stream and forming a slurry of solid sour species and hydrocarbon liquids, and a gaseous stream containing gaseous sour species;
b) separating the gaseous stream containing gaseous sour species and the slurry;

c) treating the gaseous stream containing gaseous sour species with a liquid solvent and forming a dehydrated sweetened gas stream and liquid solution of the sour species.

The term "dehydrated gas feed stream" as used herein refers to a natural gas stream that has undergone a dehydration process. Typically the dehydrated gas feed stream has a water content of less than 50 ppm, and preferably less than 7 ppm. Any suitable process for dehydrating the natural gas stream can be used. Typical examples of suitable dehydration processes include but are not limited to 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, using a dehydration process as described in WO 2004/070297.

The term "dehydrated sweetened gas stream" as used herein refers to the dehydrated gas feed stream from which sour species have been substantially removed.

Typically, the sour species comprise but are not limited to any one of, or a mixture of any two or more of, CO₂, H₂S, mercaptans, COS, CS₂, aromatic hydrocarbons and mercury.

In one embodiment, the step of cooling the dehydrated natural gas feed stream comprises adiabatically expanding the dehydrated natural gas stream. Typically, the cooling step
achieves temperature and pressure conditions at which the sour species solidifies and hydrocarbon liquids forms.

In another embodiment, the step of separating the solid sour species and the hydrocarbons liquid from the gaseous stream containing the gaseous sour species is conducted under gravity, centrifugal force, or other suitable techniques known in the art.

In one embodiment the process further comprises a step of removing the solid sour species from the slurry. In some embodiments, the step of removing the solid sour species comprises heating the slurry and melting the solid sour species, thereby forming a liquid rich in sour species. Typically, the slurry is heated to a temperature just above the melting point of the solid sour species. In one embodiment of the invention the step of heating the slurry comprises adding a warm liquid to the slurry. In an alternative embodiment, the step of heating the slurry comprises immersing a heater into the slurry. The liquid rich in sour species can then be diverted to other parts of the plant.

In one embodiment of the invention, the step of treating the gaseous stream containing gaseous sour species with the liquid solvent comprises contacting the gaseous stream containing the gaseous sour species with the liquid solvent. Typically, the liquid solvent is one in which the gaseous sour species is more soluble at the operating conditions than the natural gas stream. Suitable examples of liquid solvents
include but are not limited to NGL (natural gas liquids) condensate comprising a mixture of C2, liquefied petroleum gas components, C3 and C4 and C5+ hydrocarbon components, or other solvents including methanol, ethanol, dimethyl sulfoxide, ionic liquids including imidazolium, quaternary ammonium, pyrroldininium, pyridinium, or tetra alkylphosphonium.

In some embodiments of the invention, the step of contacting the gaseous stream containing the gaseous sour species with the liquid solvent comprises mixing the gaseous stream and the liquid solvent.

In some embodiments the process further comprises a step of separating the sour species from the liquid solution of the sour species. Typically, the liquid solution of the sour species undergoes a stripping process to separate the sour species from the liquid solution.

In a second aspect of the present invention there is provided an apparatus for removing sour species from a dehydrated natural gas stream comprising:

a vessel with a solids formation zone in fluid communication with a gas solvation zone, wherein the solids formation zone is configured to facilitate formation of a slurry of solid sour species and hydrocarbon liquids, and a gaseous stream containing gaseous sour species, and the gas solvation zone is configured to facilitate formation of a liquid solution of sour species;
an inlet for introducing the dehydrated natural gas feed stream to the solids formation zone;
   a fluid communication device configured to direct the gaseous stream containing gaseous sour species from the solids formation zone to the gas solvation zone;
   an inlet for introducing liquid solvent into the gas solvation zone;
   a first outlet for removing the liquid solution of the sour species from the gas solvation zone; and,
   a second outlet for removing a dehydrated sweetened gas stream from the gas solvation zone.

The term "solids formation zone" as used herein refers to a space defined by a first interior chamber of the vessel configured to facilitate formation of solid species therein. Alternatively, the term "solids formation zone" as used herein refers to an interior chamber of a first vessel configured to facilitate formation of solid species therein.

The term "gas solvation zone" as used herein refers to a space defined by a second interior chamber of the vessel configured to facilitate formation of a liquid solution of the sour species. Alternatively, the term "gas solvation zone" as used herein refers to an interior chamber of a second vessel configured to facilitate formation of a liquid solution of the sour species.

The apparatus further comprises a gas cooler for cooling the dehydrated natural gas feed stream entering the solids formation zone. Typically, the gas cooler comprises a gas
expander for adiabatically expanding the dehydrated natural gas feed stream, such as, for example, a Joule-Thomson valve, an orifice or venturi, a turbo expander, or a turbo expander in sequential combination with a Joule-Thomson valve. In some embodiments, the gas expander can define the inlet for introducing the dehydrated natural gas feed stream into the solids formation zone.

The step of cooling the dehydrated natural gas feed stream entering the solids formation zone is performed under conditions to facilitate formation of solid sour species and a liquid condensate of hydrocarbons. In one embodiment of the invention, the solids formation zone further comprises a collection zone into which the solid sour species and liquid concentrate collect and form a slurry. Separation may be accomplished by gravity, centrifugal force, or other suitable techniques known in the art.

The apparatus further comprises a heater disposed in the collection zone to heat the slurry and melt the solid sour species. Typically, the slurry is heated to a temperature just above the melting point of the solid sour species with the heater. Suitable examples of a heater include, but are not limited to, an immersion heater or a heat exchanger, in particular a heat exchanger tube bundle.

In an alternative embodiment, the collection zone is provided with a warm liquid inlet configured to facilitate ingress of a warm liquid into the slurry to heat the slurry and melt the sour species.
The apparatus further comprises an outlet from which the resultant liquid sour species can be removed from the collection zone.

Under certain operating conditions, the density of the liquid hydrocarbon is less than the density of liquid carbon dioxide. Thus, in some embodiments, the liquid hydrocarbon will settle under gravity above liquid sour species, such as liquid carbon dioxide. In these embodiments the apparatus further comprises an outlet from which a liquid hydrocarbon can be removed from the collection zone. Typically, in this particular embodiment the hydrocarbon outlet is disposed above the outlet from which the liquid carbon dioxide is removed in the collection zone.

The apparatus is configured to provide fluid communication between the solids formation zone and the gas solvation zone via a fluid communication device, the fluid communication device being configured to prevent return of liquid phase from the gas solvation zone to the solids formation zone. In some embodiments the fluid communication device comprises a chimney tray or a non-return valve.

In an alternative embodiment, the fluid communication device is disposed externally of the solids formation zone and the gas solvation zone with one end of the fluid communication device is in fluid communication with an upper portion of the solids formation zone and the opposing end of the fluid communication device is in fluid communication with a lower
portion of the gas solvation zone. In this particular embodiment, the fluid communication device comprises a conduit.

Location of the solids formation zone and the gas solvation zone in a single vessel is cost effective, as the footprint of the apparatus is smaller and only one pressure containing head is required. However, in alternative embodiments it may be more advantageous to locate the solids formation zone in a first vessel and to locate the gas solvation zone in a second vessel, having a fluid communication device disposed therebetween. In these alternative embodiments, the fluid communication device is disposed externally of the first and second vessels with one end of the fluid communication device in fluid communication with an upper portion of the solids formation zone of the first vessel and the opposing end of the fluid communication device is in fluid communication with a lower portion of the gas solvation zone of the second vessel. In this particular embodiment, the fluid communication device comprises a conduit.

In one embodiment, the apparatus further comprises a liquid-gas contactor disposed in the gas solvation zone. In one embodiment, the liquid-gas contactor comprises a plurality of trays or random packing or structured packing disposed in the gas solvation zone.

In one embodiment the inlet for introducing the liquid solvent into the gas solvation zone is disposed above the liquid-gas contactor. Typically, the inlet comprises a
plurality of spray nozzles or a liquid distributor. The spray nozzles or distributor maximize the contact area of the cooled liquid solvent with the dehydrated natural gas stream containing the gaseous sour species and facilitate liquid-gas contact. Accordingly, in some embodiments of the invention, the spray nozzles are also configured to comprise the liquid-gas contactor.

In one embodiment of the invention, the first outlet for removing the liquid solution of the sour species from the gas solvation zone is in fluid communication with a stripper to remove the sour species from the liquid solution and recover liquid solvent. Recirculators can be provided to recycle the recovered liquid solvent to the inlet for re-introducing recovered liquid solvent to the gas solvation zone. A liquid solvent dispenser is also provided to introduce liquid solvent makeup as necessary to maintain inventory in the circuit. The stripped sour species may be recycled back into the upstream process or otherwise disposed in the plant fuel system or as a waste product.

In prior art systems, carbon dioxide is typically removed from the dehydrated natural gas feed stream by passing it through a physical or chemical absorption unit, and then stripping the carbon dioxide from the solvent and venting to atmosphere. Alternatively, the gaseous carbon dioxide can be liquefied with costly compression processes. A substantial number of potential gas fields are not regarded as economically viable as the carbon dioxide content of the natural gas feed stream at the well head is regarded as to high to be processed, and
disposed of, economically.

The present invention is based on the realisation that it is possible to separate liquid carbon dioxide from a dehydrated natural gas feed stream. The liquid carbon dioxide can then be pumped and sequestered with relatively little energy use, as opposed to a traditional solvent absorption unit which requires costly compression equipment.

In a third aspect of the present invention there is provided a process for recovering liquid carbon dioxide from a dehydrated natural gas feed stream comprising the steps of:

a) cooling the dehydrated natural gas feed stream and forming a slurry of solid carbon dioxide particles and hydrocarbon liquids, and a gaseous stream containing gaseous carbon dioxide;

b) separating the gaseous stream containing gaseous carbon dioxide and the slurry;

c) treating the gaseous stream containing gaseous carbon dioxide with a liquid solvent and forming a liquid solution of carbon dioxide; and

d) heating the slurry and melting the solid carbon dioxide particles and forming liquid carbon dioxide.

In the claims of this application and in the description of the invention, except where the context requires otherwise due to express language or necessary implication, the words "comprise" or variations such as "comprises" or "comprising" are used in an inclusive sense, i.e. to specify the presence of the stated features, but not to preclude the presence or
addition of further features in various embodiments of the invention.

**Brief Description of the Figures**

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

- Figure 1 shows schematically a process flow diagram in accordance with one embodiment of the present invention;
- Figure 2 shows schematically a process flow diagram in accordance with an alternative embodiment of the present invention; and,
- Figure 3 shows schematically a process flow diagram in accordance with a further embodiment of the present invention.

**Detailed Description of the Preferred Embodiments of the Invention**

20 Before the preferred embodiment of the present apparatus is described, it is understood that this invention is not limited to the particular materials described, as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing the particular embodiment only, and is not intended to limit the scope of the present invention in any way. It must be noted that as used herein, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as
commonly understood by one of ordinary skill in the art to which this invention belongs.

Referring to the figures, where like numerals refer to like features throughout, in accordance with various aspects of the present invention, there is shown an apparatus 10 for performing the process of the present invention. The apparatus 10 includes a vessel 12 in which a dehydrated natural gas feed stream is treated to remove sour species therefrom.

Prior to introduction of the dehydrated natural gas feed stream into the apparatus 10, a natural gas stream from a well head or storage reservoir will be subjected to a dehydration process. The resulting dehydrated natural gas feed stream will typically have a water content of less than 50 ppm, and preferably less than 7 ppm. 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.

The temperature and pressure of the dehydrated natural gas feed stream introduced to the apparatus 10 is dependent on the upstream dehydration process employed to dehydrate the natural gas stream. For example, a dehydrated natural gas feed stream resulting from treatment with molecular sieves
can be introduced to the apparatus 10 through conduit 14 at a temperature of up to 40°C and pressure of about 70 bar.

While the preferred input pressure for the dehydrated natural gas feed stream is > 70 bar, the process and apparatus 10 of the present invention will accommodate a lower input pressure for the dehydrated natural feed gas stream if the dehydrated natural gas feed stream is pre-cooled to a temperature just above the theoretical freezing temperature of the CO$_2$ in the dehydrated gas stream.

In the embodiments shown in the figures, the dehydrated natural gas feed stream is fed through conduit 14 via a heat exchanger 16 to a flash vessel 18 in which a condensate of liquid petroleum gas (mainly comprising C3 and C4 hydrocarbons) and heavier hydrocarbons and a fraction(s) of the sour species is separated from the dehydrated natural gas stream. The condensate is then directed through conduit 20 to a condensate stabilizer or other fractionators (not shown) for further treatment to recover commercial product(s).

The pressure and temperature conditions within the flash vessel 18 would typically be in the order of 30 to 70 bar and about -15 to -40°C.

In some embodiments, further cooling of the dehydrated natural gas feed stream downstream of the heat exchanger 16 can be performed in a first refrigerated heat exchanger 70a, which is cooled by a first refrigerant such as propane or
ammonia. The refrigerant would be provided from a closed refrigeration circuit external to the apparatus 10.

The dehydrated natural gas feed stream is then directed through conduit 22 to heat exchanger 24 to cool the dehydrated natural gas feed stream to a temperature marginally greater than a temperature at which solidification of the sour species contained in the dehydrated natural gas stream occurs.

Additionally, the dehydrated natural gas feed stream can be further cooled by passing the dehydrated natural gas feed stream through a second refrigerated heat exchanger 70b located upstream of the gas expander, and which is cooled by a second refrigerant such as ethylene. The refrigerant would be provided from a closed refrigeration circuit external to the apparatus 10. In some embodiments, the first and second refrigerants may be combined in a mixed refrigeration system.

The cooled dehydrated natural gas feed stream is fed to the solids formation zone 80 of vessel 12 via inlet 28. The cooled dehydrated natural gas feed stream is expanded using a Joule-Thomson valve 26 or other suitable gas expander such as a turbo expander to further cool the stream as it enters the vessel 12. In one embodiment, the cooled dehydrated natural gas stream is expanded using a turbo expander in sequential combination with the Joule-Thomson valve 26.
In this particular embodiment, the Joule-Thomson valve 26 defines the inlet 28 for the dehydrated natural gas stream to the vessel 12.

5 The process of expanding the dehydrated natural gas feed stream upon introduction to the solids formation zone 80 of the vessel 12 achieves temperature and pressure conditions within the solids formation zone 80 at which the sour species contaminants contained in the dehydrated natural gas feed stream solidify. The process of expansion cools the dehydrated natural gas stream entering the solids formation zone 80 of the vessel 12 at inlet 28 to about -70°C to -160 °C in a pressure range of 15 to 30 bar.

15 Upon cooling the dehydrated natural gas feed stream, as described above, a small amount of liquid condensate of NGL will also form under the temperature and pressure conditions in the solids formation zone.

20 The solid sour species and the liquid condensate migrate to a lower portion 30 of the vessel 12 under gravity separation, thereby forming a slurry of natural gas liquids and solid sour species. In other embodiments, separation of the slurry from the remaining dehydrated 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.

The slurry of solid sour species is then heated to a temperature at least marginally greater than the
solidification temperature of the solid sour species to convert the solid sour species to a liquid phase in the lower portion 30 of the vessel 12 and afford a liquid stream rich in the sour species. The nature and concentration of the sour species in the liquid phase is highly dependant on the composition of the natural gas. For example, concentrations of carbon dioxide in the liquid phase can be >70%. In this embodiment, the vessel 12 is provided with an immersion heater 32 which heats the slurry up to a temperature at least marginally greater than the melting point temperature of the solid sour species. The immersion heater 32 may be a heat exchanger tube bundle which affords cooling of the inlet gas or other process streams while heating the slurry. In small volume applications, the immersion heater 32 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 the solid sour species can be introduced into the lower portion 30 of the vessel 12 and mixed with the slurry to melt the solid sour species.

The liquid stream rich in the sour species is removed from the vessel 12 through conduit 34 from outlet 96. Under processing conditions where the liquid stream is rich in liquid carbon dioxide, the liquid stream may be directly pumped through heat exchanger 16 to a liquid carbon dioxide sequestration site, or disposed of for retail sale. Under some operating conditions, the density of the liquid hydrocarbon is less than the density of liquid carbon
dioxide, and the liquid hydrocarbon can be separated from the collection zone 30 via conduit 94 from outlet 92.

Alternatively, the liquid stream may undergo one or more separation processes, typically in a fractionator (not shown), to separate the sour species from any methane or NGL condensate. In some embodiments, the fractionator can be disposed in the lowermost portion of the vessel 12. A methane-rich stream derived from fractionation may be returned to the bottom of the solid formation zone 80 or consumed as plant fuel.

If the remaining liquid stream is sufficiently rich in NGLs, these may be recovered by further fractionation. Such fractionation would necessarily produce a gaseous sour species which would require recompression and refrigeration to condense the sour species to liquid phase, or it would be incinerated and/or vented as a cold sour species gaseous stream. It is envisaged that the cold sour species gaseous stream so produced would be directed through heat exchanger 16 to cool the dehydrated natural gas stream before incineration or venting to conserve energy within the apparatus 10.

While most of the sour species in the dehydrated natural gas stream will be solidified in the solids formation zone 80, under the processing conditions of the present invention a fraction of the sour species will remain in the gas phase and be contained in the remaining dehydrated natural gas stream disposed in the solids formation zone 80, thereby comprising
a gaseous stream containing gaseous sour species. The fraction of sour species remaining in the gas phase is determined by the process conditions established within the solids formation zone and the nature and concentration of the sour species in the dehydrated natural gas feed stream.

The gaseous stream containing the gaseous sour species is directed into a gas solvation zone 90 fluid communication device, such as a chimney tray 38. In this particular embodiment, the gas solvation zone is disposed in an upper portion 36 of the vessel 12.

In an alternative embodiment shown in Figure 2, the vessel 12 is provided with a seal pan 51 comprising a solid tray extending across the vessel 12. In this configuration there is no internal fluid communication between the gas solvation zone 90 and the solids formation zone 80 within the vessel 12. In this embodiment the fluid communication device comprises a conduit 53 disposed externally of the vessel 12 in fluid communication with the solids formation zone 80 and the gas solvation zone 90. Typically, one end of the conduit 53 is in fluid communication with an upper portion of the solids formation zone 80 and the opposing end of the conduit 53 is in fluid communication with a lower portion of the gas solvation zone 90.

In a further embodiment shown in Figure 3, the solids formation zone 80 is disposed in a first vessel 12a and the gas solvation zone 90 is disposed in a second vessel 12b. In this embodiment fluid communication between the solids
formation zone 80 and the gas solvation zone 90 is facilitated by a fluid communication device comprising conduit 53 disposed externally of the first and second vessels 12, 12b. One end of the conduit 53 is in fluid communication with an upper portion of the solids formation zone 80 and the opposing end of the conduit 53 is in fluid communication with the gas solvation zone 90.

Referring to the figures, the gas solvation zone 90 is provided with a liquid-gas contactor 40. Preferably, the liquid-gas contactor 40 is selected to optimize the contact area between a cooled liquid solvent and the dehydrated natural gas stream containing the gaseous sour species. In this particular embodiment the liquid-gas contactor 40 comprises a plurality of trays or random packing or structured packing disposed in the upper portion 36 of the vessel 12.

The cooled liquid solvent is introduced into the upper portion 36 of the gas solvation zone 90 through inlet 42 disposed above the liquid-gas contactor 40. In these particular embodiments, the inlet 42 is a distributor designed to deliver liquid evenly to the liquid-gas contactor 40.

The cooled liquid solvent is selected to mix with and solvate the gaseous sour species and form a liquid solution of the gaseous sour species. Suitable examples of cooled liquid solvents in accordance with the present invention include but are not limited to NGL condensate comprising a mixture of C2,
liquefied petroleum gas components, C3 and C4 and C5+ hydrocarbon components, or other solvents including methanol, ethanol, dimethyl sulfoxide, ionic liquids including imidazolium, quaternary ammonium, pyrrolidinium, pyridinium, or tetra alkylphosphonium.

The thermodynamics of forming solids of the sour species generates heat transfer to the dehydrated natural gas stream. Advantageously, the cooled liquid solvent is introduced into the upper portion 36 of the vessel 12 in a manner which also cools the gaseous stream containing gaseous sour species directed into the gas solvation zone 90 from the solids formation zone 80.

The resulting liquid solution of the gaseous sour species collects in a lowermost portion 50 of the liquid-gas contactor 40 and is removed from the gas solvation zone 90 at outlet 55 via conduit 52.

The liquid solution of the gaseous sour species is directed via conduit 52 to heat exchanger 54 and thence to a stripper 56 comprising a fractionation column to strip the sour species, in gaseous form, from the liquid solution. The stripper 56 can be provided with an immersion heater 57 or an exterior reboiler to assist in the stripping process. The sour species is vented via conduit 58. Alternatively, the sour species can undergo recompression to condense the sour species to a liquid phase. The sour species may also be recycled through apparatus 10 to conserve energy, or consumed as fuel, or incinerated.
The stripped solvent is pumped with pump 60 via conduit 62 to heat exchanger 54 for cooling, and then to heat exchanger 48 for further cooling before reintroduction to inlet 42 in the gas solvation zone 90.

It will be understood that a liquid solvent dispenser 98 can also be provided to introduce liquid solvent make-up as necessary to maintain inventory in the circuit.

A product stream comprising dehydrated sweetened natural gas is removed from the gas solvation zone at outlet 44 via conduit 45. The product stream is at a pressure of between 15 to 30 bar and a temperature of -70°C to -100°C. A product stream with concentrations of 200 ppm CO₂, has been obtained using the process described above.

The product stream can be further cooled by expanding the gas in an expansion device 46, and the cooled product stream is used in one or more of heat exchangers 48 and 24 to cool the liquid solvent and the dehydrated natural gas feed stream, respectively, within the apparatus 10 to conserve as much energy within the apparatus 10 as possible.

It will also be evident from the description above that, as much as possible, energy is conserved within the apparatus 10, in respect of heat transfer between the liquid solution of the gaseous sour species and the product stream with recycled solvent returning to the vessel 12 from the stripping process.
Typically, as the product stream must undergo a recompression process in preparation for sale, it is envisaged that the process of the present invention will be operated at a process stream pressure which is as high as can be utilized under the operating conditions and limitations of the apparatus 10.

Numerous variations and modifications will suggest themselves to persons skilled in the relevant art, in addition to those already described, without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description.
CLAIMS

1. A process for removing a sour species from a dehydrated natural gas feed stream comprising the steps of:
   (a) cooling the dehydrated natural gas feed stream and forming a slurry of solid sour species and hydrocarbon liquids, and a gaseous stream containing gaseous sour species;
   (b) separating the gaseous stream containing gaseous sour species and the slurry; and,
   (c) treating the gaseous stream containing gaseous sour species with a liquid solvent and forming a dehydrated sweetened gas stream and a liquid solution of the sour species.

2. The process according to claim 1, wherein the step of cooling the dehydrated natural gas feed stream comprises adiabatically expanding the dehydrated natural gas feed stream.

3. The process according to claim 1 or claim 2, wherein the step of separating the solid sour species and the liquid condensate from the gaseous feed stream containing the gaseous sour species is conducted under gravity, centrifugal force, or other suitable separation techniques known in the art.

4. The process according to any one of the preceding claims, wherein the process further comprises a step of removing the solid sour species from the slurry.
5. The process according to claim 4, wherein the step of removing the solid sour species comprises heating the slurry and melting the solid sour species, thereby forming a liquid rich in sour species.

6. The process according to claim 5, wherein the slurry is heated to a temperature just above the melting point of the solid sour species.

7. The process according to claim 5 or claim 6, wherein a warm liquid is added to the slurry.

8. The process according to claim 5 or claim 6, wherein a heater is immersed in the slurry.

9. The process according to any one of the preceding claims, wherein the step of treating the gaseous stream containing gaseous sour species with the liquid solvent comprises contacting the gaseous stream containing the gaseous sour species with the liquid solvent.

10. The process according to any one of the preceding claims, wherein the step of contacting the gaseous stream containing the gaseous sour species with the liquid solvent facilitates forming a liquid solution of the sour species in the liquid solvent.

11. The process according to any one of the preceding claims, wherein the liquid solvent comprises a solvent in
which the gaseous sour species is more soluble than in the natural gas stream.

12. The process according to any one of the preceding claims, wherein the liquid solvent comprises any one of methanol, ethanol, dimethyl sulfoxide, ionic liquids selected from a group comprising imidazolium, quaternary ammonium, pyrrolidinium, pyridinium, or tetra alkylphosphonium, or a NGL [natural gas liquids] condensate comprising a mixture of C2, liquefied petroleum gas components, C3 and C4 and C5+ hydrocarbon components, or a combination thereof.

13. The process according to any one of the preceding claims, wherein the process further comprises a step of separating the gaseous sour species from the liquid solution of the sour species.

14. The process according to claim 13, wherein the liquid solution of the gaseous sour species undergoes a stripping process to separate the sour species from the liquid solution.

15. The process according to any one of the preceding claims, wherein the sour species comprises any one of, or a mixture of any two or more of, CO₂, H₂S, mercaptans, COS, CS₂, aromatic hydrocarbons and mercury.

16. An apparatus for removing a sour species from a dehydrated natural gas feed stream comprising:
a vessel with a solids formation zone in fluid communication with a gas solvation zone, wherein the solids formation zone is configured to facilitate formation of a slurry of solid sour species and hydrocarbon liquids, and a gaseous feed stream containing gaseous sour species, and the gas solvation zone is configured to facilitate formation of a liquid solution of sour species;

an inlet for introducing the dehydrated natural feed gas stream to the solids formation zone;

a fluid communication device configured to direct the gaseous stream containing gaseous sour species from the solids formation zone to the gas solvation zone;

an inlet for introducing liquid solvent into the gas solvation zone;

a first outlet for removing the liquid solution of the sour species from the gas solvation zone; and,

a second outlet for removing a dehydrated sweetened gas product stream from the gas solvation zone.

17. The apparatus according to claim 16, wherein the solids formation zone is disposed in a first vessel and the gas solvation zone is disposed in a second vessel.

18. The apparatus according to claim 16 or claim 17, wherein the apparatus further comprises a gas cooler for cooling the dehydrated natural gas feed stream entering the solids formation zone.
19. The apparatus according to claim 18, wherein the gas cooler comprises a gas expander for adiabatically expanding the dehydrated natural gas feed stream.

20. The apparatus according to claim 19, wherein the gas expander comprises a Joule-Thomson valve, an orifice or venturi, a turbo expander, or a turbo expander in sequential combination with a Joule-Thomson valve.

21. The apparatus according to claim 19 or claim 20, wherein the gas expander defines the inlet for introducing the dehydrated natural gas feed stream into the solids formation zone.

22. The apparatus according to any one of claims 16 to 21, wherein the solids formation zone further comprises a collection zone into which the solid sour species and liquid concentrate collect and form a slurry.

23. The apparatus according to claim 22, wherein the apparatus further comprises a heater disposed in the collection zone to heat the slurry and melt the solid sour species.

24. The apparatus according to claim 23, wherein the heater comprises an immersion heater or a heat exchanger.

25. The apparatus according to claim 22, wherein the collection zone is configured to facilitate ingress of a warm
liquid into the slurry to heat the slurry and melt the solid sour species.

26. The apparatus according to any one of claims 23 to 25, wherein the apparatus further comprises an outlet from which the liquid sour species can be removed from the collection zone.

27. The apparatus according to any one of claims 22 to 26, wherein the apparatus further comprises an outlet from which the liquid hydrocarbon can be removed from the collection zone.

28. The apparatus according to claim 27, wherein the outlet from which the liquid hydrocarbon can be removed is disposed above the outlet from which the liquid sour species can be removed.

29. The apparatus according to any one of claims 16 to 28, wherein the apparatus is configured to provide fluid communication between the solids formation zone and the gas solvation zone via a fluid communication device, the fluid communication device being configured to prevent return of liquid phase from the gas solvation zone to the solids formation zone.

30. The apparatus according to claim 29, wherein the fluid communication device comprises a chimney tray or a non-return valve.
31. The apparatus according to any one of claims 16 to 30, wherein the apparatus further comprises a liquid-gas contactor disposed in the gas solvation zone.

32. The apparatus according to claim 31, wherein the liquid-gas contactor comprises a plurality of trays or random packing or structured packing disposed in the gas solvation zone.

33. The apparatus according to claim 31 or claim 32, wherein the inlet for introducing the liquid solvent into the gas solvation zone is disposed above the liquid-gas contactor.

34. The apparatus according to any one of claims 16 to 33, wherein the inlet comprises a plurality of spray nozzles or a liquid distributor.

35. The apparatus according to any one of claims 16 to 34, wherein the first outlet for removing the liquid solution of the sour species from the gas solvation zone is in fluid communication with a stripper to remove the sour species from the liquid solution and recover liquid solvent.

36. The apparatus according to claim 35, wherein the apparatus further comprises a recirculator to recycle the recovered liquid solvent to the inlet for introducing liquid solvent to the gas solvation zone.

37. A process for recovering liquid carbon dioxide from a dehydrated natural gas feed stream comprising the steps of:
(a) cooling the dehydrated natural gas feed stream and forming a slurry of solid carbon dioxide particles and hydrocarbon liquids, and a gaseous stream containing gaseous carbon dioxide;

(b) separating the gaseous stream containing gaseous carbon dioxide and the slurry;

(c) treating the gaseous stream containing gaseous carbon dioxide with a liquid solvent and forming a liquid solution of carbon dioxide; and,

(d) heating the slurry and melting the solid carbon dioxide particles and forming liquid carbon dioxide.