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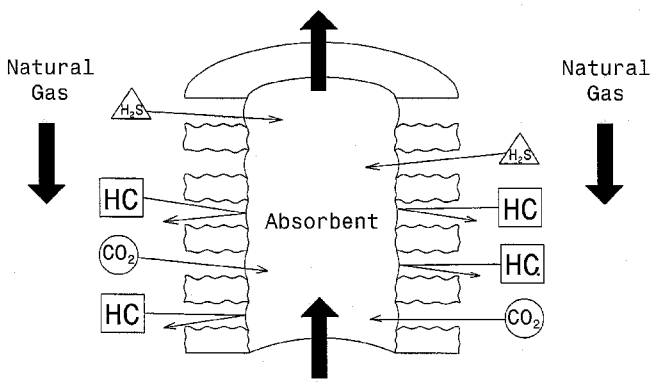

Fig. 1A

(57) Abstract: The present disclosure relates to natural gas purification. More particularly, the present disclosure relates to a system and process for removing impurities from a natural gas stream in a floating environment, such as on a ship or barge, which carries a membrane contactor that includes at least one hydrophobic membrane module having a plurality of PTFE hollow fiber membranes (e.g., including or consisting of microporous PTFE membranes).

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A NATURAL GAS PURIFICATION SYSTEM AND A PROCESS OF USING THEREOF

TECHNICAL FIELD

The present disclosure relates to natural gas purification. More particularly, the present disclosure relates to a system and process for removing impurities from natural gas in a floating environment, such as on a ship or barge.

BACKGROUND

Petroleum reservoirs can be found onshore and/or offshore. There has been an interest in Floating Liquefied Natural Gas (FLNG) systems as a way to develop stranded gas reservoirs that are isolated and remote from land. These isolated and remote reservoirs generally are too small for permanent platform installation. An FLNG system can use a ship or barge to house necessary recovery, gas treatment, liquefaction and offloading equipment.

Compared to a land based Liquefied Natural Gas (LNG) plant, an FLNG system will typically have a greater need for a modular design to minimize the equipment footprint, equipment weight and equipment space requirement.

An additional challenge for FLNG systems is the effect of sea motion on the performance of processing equipment, especially for systems containing liquid (e.g., amine solvent systems).

In general, the currently known natural gas purification systems for offshore fixed and floating applications are relatively large and, thus, can be economically and structurally disadvantageous for FLNG applications where there are stringent limitations on space and weight allocated to the natural gas purification process. Also, the currently known natural gas purification systems for offshore fixed and floating applications typically exhibit a relatively large degree of methane loss coupled with the reduction in carbon dioxide content.

In FLNG systems and processes where natural gas is cooled to a very low temperature of about -160°C, carbon dioxide content in the feed gas stream must typically be reduced to less than about 50 ppmv before liquefaction to avoid formation of dry ice within the liquefaction system.

For offshore fixed and floating platforms, membrane systems including dry membrane systems have typically been selected for reducing carbon dioxide content. Membrane systems and processes are generally based on solution-diffusion technology. Carbon dioxide can diffuse from the natural gas feed stream from one side of the membrane to the other side of the membrane. However, some hydrocarbons such as methane, ethane, propane and butane can also diffuse from the natural gas feed stream according to the same principle as carbon dioxide. The majority of hydrocarbon loss comes from the loss of methane.

For conventional membrane systems including dry membrane systems, a single stage unit typically exhibits about 20% hydrocarbon loss. Depending on the type of membrane system used, about 10% to about 20% of the hydrocarbon loss is based on methane loss. To prevent methane loss, some operators of conventional membrane systems and processes install a second stage unit. However, even with the addition of a second stage unit, the conventional membrane systems and processes still exhibit a relatively large amount of methane loss.

Thus, there exists a need for an improved compact and robust natural gas purification system and process of using thereof for FLNG applications that can remove carbon dioxide to meet FLNG requirements with minimal methane loss.

SUMMARY

A first aspect of the present disclosure provides a process for treating a natural gas stream, that can comprise: directing the natural gas stream to an offshore platform, wherein the offshore platform comprises a hybrid gas-liquid contact system; directing the natural gas stream to the hybrid gas-liquid contact system, wherein the hybrid gas-liquid contact system comprises a membrane contactor and a solvent; removing acid gases (such as carbon dioxide (CO_2) and/or hydrogen sulfide (H_2S)) from the natural

gas stream to produce a purified natural gas stream and removed CO_2; wherein the membrane contactor comprises a hydrophobic membrane module.

In some embodiments, the hydrophobic membrane module can comprise a plurality of hollow fiber membranes (e.g., microporous membranes). In some embodiments, the hydrophobic membrane module can comprise a bundle of hollow fiber membranes. In some embodiments, the hydrophobic membrane module can comprise a plurality of hollow fiber membranes, wherein the plurality of hollow fiber membranes can comprise a bundle of hollow fiber membranes. In some embodiments, the hydrophobic membrane module can comprise a cylindrical shape. In some embodiments, one or more of the plurality of hollow fiber membranes can comprise polytetrafluoroethylene (PTFE). In some embodiments, each of the plurality of hollow fiber membranes can comprise PTFE.

In some embodiments, each of the plurality of hollow fiber membranes can have an inner diameter of about 0.1 mm to about 2 mm. In some embodiments, each of the plurality of hollow fiber membranes can have a wall thickness of about 1% of the inner diameter to about 50% of the inner diameter.

In some embodiments, the number and/or amount of hollow fiber membranes present in the hydrophobic membrane module is dependent on the packing density of the hydrophobic membrane module. The packing density is the ratio of an area corresponding to the plurality of hollow fiber membranes (e.g., the bundle of hollow fiber membranes) among a cross-sectional area of the hydrophobic membrane module to the cross-sectional area of the hydrophobic membrane module. In some embodiments, the hydrophobic membrane module comprises a packing density of about 0.3 cm^2/cm^2 to about 0.7 cm^2/cm^2.

In some embodiments, each of the plurality of hollow fiber membranes can comprise a porosity of about 30% to about 70%.

In some embodiments, the plurality of hollow fiber membranes can be bundled together and/or held in place in accordance with a predetermined spatial organization or pattern (e.g., an array) using a material such as a perfluoroalkoxy (PFA). In some embodiments, the plurality of hollow fiber membranes can be bundled together and/or held in place using a material such as perfluoroalkoxy (PFA) tubing. In some embodiments, the plurality of hollow fiber membranes can be bundled together and/or held in place using a material such as an epoxy. Other materials are also suitable for bundling and/or holding the PTFE hollow fiber membranes together / in place.

In some embodiments, the hydrophobic membrane module comprises a case and/or casing. In some embodiments, the casing can comprise a material such as an acrylic. In some embodiments, the casing can comprise a material such as a perfluoroalkoxy (PFA). Other materials are also contemplated.

In some embodiments, the solvent can comprise water, sea water, brackish water, an amine solvent or a combination of one or more thereof. In some embodiments, the solvent can comprise an amine solvent.

In some embodiments, the purified natural gas stream can comprise CO_2 in an amount of less than about 50 ppmv. In some embodiments, the purified natural gas stream can comprise CO_2 in an amount of about 40 ppmv or less. In some embodiments, the purified natural gas stream can comprise CO_2 in an amount of about 30 ppmv or less. In some embodiments, the purified natural gas stream can comprise CO_2 in an amount of about 23 mole % or less.

In some embodiments, the purified natural gas stream can comprise H_2S in an amount of less than about 50 ppmv. In some embodiments, the purified natural gas stream can comprise H_2S in an amount of 10 ppmv or less. In some embodiments, the purified natural gas stream can comprise H_2S in an amount of 5 ppmv or less. In some embodiments, the purified natural gas stream can comprise H_2S in an amount of about 0 ppmv.

In some embodiments, the process can result in a loss of methane in an amount of about 7 mole % or less. In some embodiments, the process can result in a loss of methane in an amount of about 5 mole % or less. In some embodiments, the process can result in a loss of methane in an amount of about 3 mole % or less. In some embodiments, the process can result in a loss of methane in an amount of about 2 mole % or less. In some embodiments, the process can result in a loss of methane in an amount of about 1 mole % or less.

In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in an amine solvent and/or withstand an amine solvent for at least 18 months. In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in an amine solvent and/or withstand an amine solvent for at least 24 months.

In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in high temperatures and/or withstand high temperatures of up to about 120 degrees Celsius. In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in high temperatures and/or withstand high temperatures of up to about 150 degrees Celsius.

In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can exhibit improved stability in an absorption system and desorption system.

In some embodiments, the process can result in a reduced amine solvent equipment footprint in comparison with conventional amine systems by about 40% or more.

In some embodiments, the process can result in a decrease in capital expenditures in comparison to conventional amine systems by about 42% or more.

In some embodiments, the offshore platform can comprise a fixed offshore platform. In some embodiments, the fixed offshore platform can comprise a pipeline.

In some embodiments, the offshore platform can comprise a floating offshore platform. In some embodiments, the floating offshore platform can comprise a floating liquefied natural gas (FLNG) system. In some embodiments, the FLNG system can comprise a ship or barge.

A second aspect of the present disclosure provides a hybrid gas-liquid contact system for an offshore platform, wherein the hybrid gas-liquid contact system comprises: a membrane contactor and a solvent; wherein the membrane contactor comprises a hydrophobic membrane module.

In some embodiments, the hydrophobic membrane module can comprise a plurality of hollow fiber membranes. In some embodiments, the hydrophobic membrane module can comprise a bundle of hollow fiber membranes (e.g., microporous membranes). In some embodiments, the hydrophobic membrane module can comprise a cylindrical shape. In some embodiments, one or more of the plurality of hollow fiber membranes can comprise polytetrafluoroethylene (PTFE). In some embodiments, each of the plurality of the hollow fiber membranes can comprise PTFE.

In some embodiments, the solvent can comprise water, sea water, brackish water, an amine solvent or a combination of one or more thereof. In some embodiments, the solvent can comprise an amine solvent.

In some embodiments, the hybrid gas-liquid contact system can reduce a carbon dioxide (CO_2) content in a natural gas stream to less than about 50 ppmv. In some embodiments, the hybrid gas-liquid contact system can reduce the CO_2 content in the natural gas stream to about 40 ppmv or less. In some embodiments, the hybrid gas-liquid contact system can reduce the CO_2 content in the natural gas stream to about 30 ppmv or less. In some embodiments, the hybrid gas-liquid contact system can reduce the CO_2 content in the natural gas stream to about 23 mole % or less.

In some embodiments, the hybrid gas-liquid contact system can reduce a H_2S content in a natural gas stream to less than about 50 ppmv. In some embodiments, the hybrid gas-liquid contact system can reduce the H_2S content in the natural gas stream to about 10 ppmv or less. In some embodiments, the hybrid gas-liquid contact system can reduce the H_2S content in the natural gas stream to about 5 ppmv or less. In some embodiments, the hybrid gas-liquid contact system can reduce the H_2S content in the natural gas stream to about 0 ppmv.

In some embodiments, the hybrid gas-liquid contact system can provides a loss of methane in an amount of about 7 mole % or less. In some embodiments, the hybrid gas-liquid contact system can provide a loss of methane in an amount of about 5 mole % or less. In some embodiments, the hybrid gas-liquid contact system can provide a loss of methane in an amount of about 3 mole % or less. In some embodiments, the hybrid gas-liquid contact system can provide a loss of methane in an amount of about 2 mole % or less. In some embodiments, the hybrid gas-liquid contact system can provide a loss of methane in an amount of about 1 mole % or less.

In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in an amine solvent and/or withstand an amine solvent for at least 18 months. In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintains its stability in an amine solvent and/or withstand an amine solvent for at least 24 months.

In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in high temperatures and/or withstand high temperatures of up to 120 degrees Celsius. In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can maintain its stability in high temperatures and/or withstand high temperatures of up to about 150 degrees Celsius.

In some embodiments, each of the plurality of PTFE hollow fiber membranes and/or the PTFE hollow fiber membrane module can exhibit improved stability in an absorption system and desorption system.

In some embodiments, the hybrid gas-liquid contact system can provide a reduced amine solvent equipment footprint in comparison with conventional amine systems by about 40% or more.

In some embodiments, the hybrid gas-liquid contact system can provide a decrease in capital expenditures in comparison to conventional amine systems by about 42% or more.

In some embodiments, the offshore platform can comprise a fixed offshore platform. In some embodiments, the fixed offshore platform can comprise a pipeline.

In some embodiments, the offshore platform can comprise a floating offshore platform. In some embodiments, the floating offshore platform can comprise a floating liquefied natural gas (FLNG) system. In some embodiments, the FLNG system can comprise a ship or barge.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present disclosure are described herein with reference to the drawings in which:

FIGs. 1A-1B illustrate a cross-section view of a hollow fiber/hollow fiber membrane of a hollow fiber membrane contactor in accordance with an embodiment of the present disclosure, wherein the hollow fiber/hollow fiber membrane of the hollow fiber membrane contactor can have two modes of operation. **FIG. 1A** illustrates a first mode of operation wherein the solvent can flow on and/or along the inside/inner surface of the hollow fiber/hollow fiber membrane. **FIG. 1B** illustrates a second mode of operation wherein the solvent can flow on and/or along the outside/outer surface of the hollow fiber/hollow fiber membrane.

FIGs. 2A-2C illustrate mass transfer resistances in a series model comprising of a: **FIG. 2A)** non-wetted mode of operation example; **FIG. 2B)** fully wetted mode of operation example; and **FIG. 2C)** partially wetted mode of operation example.

DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments can be utilized, and other changes can be made, without departing from the spirit or scope of the subject matter presented herein.

Unless specified otherwise, the terms "comprising" and "comprise" as used herein, and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, un-recited elements.

As used herein, the term "about" or “approximately”, in the context of concentrations of components, conditions, other measurement values, etc., means +/- 10% of the stated

value or value range, +/- 5% of the stated value or value range, or +/- 4% of the stated value or value range, or +/- 3% of the stated value or value range, or +/- 2% of the stated value or value range, or +/- 1% of the stated value or value range, or +/- 0.5% of the stated value or value range, or +/- 0% of the stated value or value range.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6. This applies regardless of the breadth of the range.

The present disclosure relates to a natural gas purification system and process for using thereof for Floating Liquefied Natural Gas (FLNG) system applications, wherein the natural gas purification system is based on membrane contactor technology and/or gas-liquid membrane contactor technology. The membrane contactor and/or gas-liquid membrane contactor of the present disclosure combine the advantages and/or benefits of the membrane system and process, and an amine system and process.

The membrane contactor and/or gas-liquid membrane contactor of the present disclosure includes or uses a membrane or membrane structure, for instance, a hollow fiber membrane or membrane structure, instead of packing in a conventional amine based packed column/tower to increase the surface contact area. A hollow fiber membrane or membrane structure in accordance with some embodiments of the present disclosure can be microporous, for instance, having pore sizes of less than or equal to approximately 1 μm (e.g., pore sizes of approximately 1 μm). Microporosity can facilitate or result in higher flow rates and/or lower cost compared to nanoporous membranes.

In some embodiments, the overall volumetric gas-phase mass transfer coefficient (KGa) for the membrane contactor and/or gas-liquid membrane contactor of the present disclosure can be up to four (4) times larger than the value obtained from a packed column. In some embodiments, the overall volumetric gas-phase mass transfer coefficient (KGa) for the membrane contactor and/or gas-liquid membrane contactor of the present disclosure can be up to five (5) times larger than the value obtained from a packed column. In some embodiments, the overall volumetric gas-phase mass transfer coefficient (KGa) for the membrane contactor and/or gas-liquid membrane contactor of the present disclosure can be up to seven (7) times larger than the value obtained from a packed column.

The membrane contactor and/or gas-liquid membrane contactor of the present disclosure can also overcome methane loss exhibited by conventional dry membrane systems and processes by reducing methane loss. The reduction in methane loss can be achieved because the membrane contactor and/or gas-liquid membrane contactor process of the present disclosure utilizes an absorption process. The absorption process of the membrane contactor and/or gas-liquid membrane contactor process of the present disclosure is completely different from the solution-diffusion theory. The absorption process of the present disclosure can result in a loss of methane, but the amount lost is very small. The methane loss of the absorption process of the present disclosure results from the physical solubility between the solvent and methane.

In accordance with an embodiment of the present disclosure, the membrane contactor and/or gas-liquid membrane contactor can provide for a reduction in methane loss from the natural gas feed stream in comparison to conventional dry membrane systems and processes. For conventional dry membrane systems, a single stage unit typically exhibits about 10 mole % to about 20 mole % methane loss.

In accordance with an embodiment of the present disclosure, the membrane contactor and/or gas-liquid membrane contactor can provide for a reduced weight in comparison

to a conventional amine based packed column/tower and a reduced equipment footprint in comparison to a conventional amine based packed column/tower.

In accordance with an embodiment of the present disclosure, this membrane contactor and/or gas-liquid membrane contactor can be used for FLNG applications. The FLNG gas specification requires an ultra-low CO_2 concentration (e.g., compared to a conventional Liquefied Natural Gas (LNG) production procedure). The CO_2 concentration requirement for FLNG applications is about 50 ppmv, which conventional dry membrane systems and processes typically cannot meet.

In general, a conventional amine based packed column/tower is not suitable for FLNG applications because the height of the column/tower is relatively high and the size of equipment is relatively large thus requiring a large ship area which in turn would undesirably increase the capital expenditures and operational costs.

In accordance with an embodiment of the present disclosure, the membrane of the membrane contactor and/or gas-liquid membrane contactor acts as a selective barrier between gases (e.g., natural gas) and liquid (e.g., solvent). The CO_2 from a natural gas feed stream diffuses in, into, or through the membrane pores and then is absorbed by the solvent. In some embodiments, the solvent can comprise water, sea water, brackish water, and/or an amine solvent.

In some embodiments, the amine solvent can comprise monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), methyldiethanolamine (MDEA), activated-MDEA (aMDEA), 2-amino-2-methy-1-propanol (AMP) or a combination of two or more thereof.

Typically, the amine based solvent can absorb more CO_2 than a water-based solvent because the amine based solvent system and process utilizes chemical absorption.

In some embodiments, the amine solvent based system of the membrane contactor and/or gas-liquid membrane contactor can be a closed-loop system because the amine

solvent can be regenerated. When acid gases such as CO_2 and H_2S react with the amine the reaction is a reversible reaction. When the reacted amine reaches a certain temperature the acid gases can be separated from the amine.

Once the amine solvent absorbs CO_2, the amine solvent can be sent or directed to another unit known as a membrane desorber to heat the amine solvent. The heated amine solvent can then desorb CO_2 from the amine solvent. The treated amine solvent can then be sent back to the membrane contactor and/or gas-liquid membrane contactor of the present disclosure, which can also be referred to as a membrane absorber unit.

On the other hand, if the solvent is water, sea water and/or brackish water the mechanism for CO_2 absorption is physical absorption. For example, the physical absorption is based on the solubility of water and CO_2. After CO_2 is absorbed by water in the membrane absorber unit the CO_2 rich water (e.g., water saturated with CO_2) can be sent to a flash unit to desorb CO_2 from the CO_2 rich water. The solubility of CO_2 decreases when the pressure is reduced. The flash unit can be used to reduce the pressure and the treated water can then be drained back to the sea. Draining the treated water back to sea provides for a reduced equipment footprint, reduced equipment size, and reduced equipment space requirement. For example, the size of tank(s) for storing water can be reduced. The use of water, sea water and/or brackish water as the solvent and/or the draining of treated water back to sea can provide for a reduction in the ship size requirement and a reduction in the footprint of the whole membrane contactor and/or gas-liquid membrane contactor system and process of the present disclosure.

Membrane Contactor

In accordance with an embodiment of the present disclosure, the hollow fiber membranes used in the membrane contactor and/or gas-liquid membrane contactor system and process can be hydrophobic membranes. In some embodiments, the higher the hydrophobicity of the hollow fiber membrane, the better the long-term performance of the hollow fiber membrane. In other words, the higher the hydrophobicity of the hollow fiber membrane, the greater the stability of the hollow fiber membrane. In

general, the definition of hydrophobic is that the contact angle between a water droplet and surface is higher than 90°.

In some embodiments, the hollow fiber membranes can comprise polytetrafluoroethylene (PTFE). In some embodiments, the PTFE hollow fiber membranes exhibit hydrophobic characteristics and hydrophobic polymer properties.

FIGS. 1A-1B illustrate a cross-section view of a PTFE hollow fiber/PTFE hollow fiber membrane of a PTFE hollow fiber membrane contactor in accordance with an embodiment of the present disclosure. As indicated in **FIGs. 1A – 1B**, a PTFE hollow fiber membrane or membrane structure in accordance with an embodiment of the present disclosure can have an interlamellar structure, in a manner readily understood by one having ordinary skill in the art. The PTFE hollow fiber / PTFE hollow fiber membrane of the PTFE hollow fiber membrane contactor can be configured or designed to have pore sizes that enable the passage of CO_2 and H_2S therethrough (and into the absorbent / solvent), but which block, essentially block, or very substantially block the passage of hydrocarbons (HC) therethrough.

As also indicated in **FIGs. 1A – 1B**, the PTFE hollow fiber/PTFE hollow fiber membrane of the PTFE hollow fiber membrane contactor can have two modes of operation with respect to the flow of an absorbent or solvent (e.g., received or introduced from an absorbent / solvent feed system or apparatus) relative to the flow of natural gas (e.g., received, obtained, or introduced from a natural gas source or reservoir, and directed or introduced to an FLNG platform and into the PTFE hollow fiber membrane contactor). **FIG. 1A** illustrates a first mode of operation wherein the solvent can flow on and/or along the inside/inner surface of the PTFE hollow fiber membrane. **FIG. 1B** illustrates a second mode of operation wherein the solvent can flow on and/or along the outside/outer surface of the PTFE hollow fiber membrane. Because the inside/inner surface and outside/outer surface of the PTFE hollow fiber membrane are both hydrophobic, a solvent can flow inside and/or outside the PTFE hollow fiber membrane. That is, a given PTFE hollow fiber membrane or PTFE hollow fiber membrane structure or module in accordance with an embodiment of the present

disclosure can be employed in a system configured for solvent flow on the inside of the PTFE hollow fiber membrane, or solvent flow on the outside of the PTTE hollow fiber membrane, depending upon embodiment details.

On the other hand, hydrophilic hollow fiber membranes such as a poly(ether ether ketone) (PEEK) membrane typically require the outside/outer surface of the PEEK membrane to be coated with a material to modify the outside/outer surface of the PEEK membrane such that the outside/outer surface comprises hydrophobic properties. However, since only the outside/outer surface of the PEEK membrane comprises hydrophobic properties, a solvent can only flow on and/or along the outside/outer surface of the PEEK hollow fiber membrane. The solvent must contact the hydrophobic side of the membrane to prevent membrane wetting. Membrane wetting results in water and/or solvent filled membrane pores, which in turn leads to a reduced mass transfer coefficient as can be seen in **FIG. 2A-2C**.

FIGS. 2A-2C illustrate mass transfer resistances in a series model comprising of a: **FIG. 2A**) non-wetted mode of operation example; **FIG. 2B**) fully wetted mode of operation example; and **FIG. 2C**) partially wetted mode of operation example.

FIG. 2A illustrates a non-wetted mode of operation. In the non-wetted mode of operation only the gas phase is in the membrane pores. The non-wetted mode of operation can be the most effective mode of operation for the hydrophobic hollow fiber membrane contactor of the present disclosure. The gas diffusivity in the gas phase is much larger that the gas diffusivity in the liquid phase. This leads to a high mass transfer rate in the non-wetted mode.

FIG. 2B illustrates a fully wetted mode of operation. In the fully wetted mode the liquid phase fills all the membrane pores. **FIG. 2C** illustrates a partially wetted mode of operation. In the partially wetted mode the liquid phase partially fills the membrane pores. The fully wetted mode of operation and the partially wetted mode of operation lead to a reduction in the mass transfer rate compared to the non-wetted mode of operation.

The hollow fiber membrane contactor and/or gas-liquid hollow fiber membrane contactor of the present disclosure can comprise a hollow fiber membrane module. The hollow fiber membrane module can comprise a plurality of hollow fiber membranes. The plurality of hollow fiber membranes can comprise a bundle of hollow fiber membranes.

The hollow fiber membrane module can be provided and/or prepared on a commercial scale. In some embodiments, the plurality of hollow fiber membranes and/or the hollow fiber membrane module can comprise a specific surface area of about 1 cm^2/cm^3 to about 100 cm^2/cm^3. In some embodiments, the plurality of hollow fiber membranes and/or the hollow fiber membrane module can comprise a specific surface area of greater than 100 cm^2/cm^3. In some embodiments, the bundle of hollow fiber membranes can comprise a specific surface area of about 1 cm^2/cm^3 to about 100 cm^2/cm^3. In some embodiments, the bundle of hollow fiber membranes can comprise a specific surface area of greater than 100 cm^2/cm^3.

In some embodiments, each of the plurality of hollow fiber membranes can have an inner diameter of about 0.1 mm to about 2 mm. In some embodiments, each of the plurality of hollow fiber membranes can have a wall thickness of about 1% of the inner diameter to about 50% of the inner diameter.

In some embodiments, the number and/or amount of hollow fiber membranes present in the hydrophobic membrane module is dependent on the packing density of the hydrophobic membrane module. The packing density is the ratio of an area corresponding to the plurality of hollow fiber membranes (e.g., the bundle of hollow fiber membranes) among a cross-sectional area of the hydrophobic membrane module to the cross-sectional area of the hydrophobic membrane module. In some embodiments, the hydrophobic membrane module comprises a packing density of about 0.3 cm^2/cm^2 to about 0.7 cm^2/cm^2.

In some embodiments, each of the plurality of hollow fiber membranes can comprise a porosity of about 30% to about 70%.

In some embodiments, the plurality of hollow fiber membranes corresponding to a module can be bundled together and/or held in place using a material such as a perfluoroalkoxy (PFA). In some embodiments, the plurality of hollow fiber membranes can be bundled together and/or held in place using a material such as perfluoroalkoxy (PFA) tubing. In some embodiments, the plurality of hollow fiber membranes can be bundled together and/or held in place using a material such as an epoxy. Other materials are also suitable for bundling or holding the hollow fiber membranes in place.

In some embodiments, the hydrophobic membrane module comprises a case and/or casing. In some embodiments, the casing can comprise a material such as an acrylic. In some embodiments, the casing can comprise a material such as a perfluoroalkoxy (PFA). Other materials are also contemplated.

Fluid

Aspects of the present disclosure relate to the capture or removal of CO_2 and/or H_2S from natural gas. In principle, a liquid/solvent will absorb CO_2 and/or H_2S. In accordance with an embodiment of the present disclosure, the liquid/solvent used for absorbing CO_2 and/or H_2S from a natural gas feed stream can comprise water, sea water, brackish water, an amine aqueous based solution or a combination of one or more thereof. In some embodiments, the amine aqueous based solution can comprise the amine in an amount of about 1 weight percent to up to about 40 weight percent.

Typically, each country has a specification for the concentration of CO_2 allowed in a gas pipeline or allowed for specific applications. In general, for LNG applications, the CO_2 content and/or concentration must be less than 50 ppmv.

Advantages of PTFE over PEEK

A PEEK membrane is originally a hydrophilic membrane that must be treated or modified to have hydrophobic properties. More particularly, a PEEK membrane is

treated and/or modified using a grafting process to provide hydrophobic properties. In the grafting process, the surface of the PEEK membrane is grafted with a specific material to make the PEEK membrane hydrophobic. Unfortunately, the grafting process can result in uncertainty with respect to whether the PEEK membrane surface has been effectively modified. For example, during the grafting process, a surface modification reaction may not occur at some locations or areas of the PEEK membrane's surface. Such un-modified PEEK membrane surface locations or areas remain hydrophilic, resulting in membrane wetting in the membrane contactor, thereby significantly decreasing overall mass transfer.

Furthermore, the material(s) used to coat the PEEK membrane and impart hydrophobic properties to the PEEK membrane can be susceptible to deformation and cannot be guaranteed to withstand or reliably withstand the high pressure, high temperature, high flow rate of liquid, and/or long term exposure to an amine solvent, associated with membrane contactors and/or gas-liquid contactors, especially for FLNG applications.

Moreover, the grafting process is an additional process that the PEEK membrane is required to undergo before it can be used in the membrane contactor. Thus, the grafting process can involve additional materials, additional equipment, additional time, and/or extra costs. In contrast, the PTFE hollow fiber membranes in accordance with embodiments of the present disclosure do not require an additional treatment process and/or additional modification process, as the PTFE hollow fiber membranes inherently exhibit hydrophobic properties. The PTFE hollow fiber membranes in accordance with embodiments of the present disclosure thus do not exhibit the aforementioned drawbacks associated with PEEK membranes.

Methane loss of 2 mole % (less than 7 mole %)

The conventional dry membrane systems and processes (e.g., gas permeation systems and processes) typically result in a loss of methane from the natural gas feed stream in an amount of up to about 20 mole %.

In accordance with an embodiment of the present disclosure, the use of the membrane contactor and/or gas-liquid contactor results in loss of methane from an natural gas feed stream in an amount of about 7 mole % or less, about 6 mole % or less, about 5 mole % or less, about 4 mole % or less, about 3 mole % or less, about 2 mole % or less, about 1 mole % or less, or about 0 mole %. The membrane contactor and/or gas-liquid contactor of the present disclosure utilizes an absorption process and is based on the absorption theory. As such, the membrane contactor and/or gas-liquid contactor of the present disclosure is different from conventional dry membrane systems and processes. Any methane loss exhibited in the membrane contactor process and gas-liquid contactor process of the present disclosure results from the methane that is absorbed in the liquid/solvent (e.g., water, sea water, brackish water and/or amine solvent).

REPRESENTATIVE APPLICATION

The natural gas purification system and process of the present disclosure can be used for removing impurities from natural gas received by or being treated on an offshore platform. The offshore platform can be a fixed offshore platform or a floating platform.

In a non-limiting representative example, the natural gas purification system and process of the present disclosure can be used for removing impurities from natural gas in a floating environment, for instance, on a ship or barge (e.g., a floating platform analogous, similar, or generally similar to the Royal Dutch Shell Prelude platform or another type of floating platform).

While various aspects and embodiments have been disclosed herein, it will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit of the invention being indicated by the appended claims.

We Claim:

1. A process for treating a natural gas stream, comprising:

directing the natural gas stream to an offshore platform, wherein the offshore platform comprises a hybrid gas-liquid contact system;

directing the natural gas stream to the hybrid gas-liquid contact system, wherein the hybrid gas-liquid contact system comprises a membrane contactor and a solvent;

removing carbon dioxide (CO_2) from the natural gas stream to produce a purified natural gas stream and removed CO_2;

wherein the membrane contactor comprises a hydrophobic membrane module.

2. The process of claim 1, wherein the hydrophobic membrane module comprises a plurality of hollow fiber microporous membranes.

3. The process of claim 2, wherein each of the plurality of hollow fiber membranes comprises polytetrafluoroethylene (PTFE).

4. The process of any one of claims 1-3, wherein the solvent is selected from the group consisting of water, sea water, brackish water, an amine solvent or a combination of one or more thereof.

5. The process of any one of claims 1-4, wherein the solvent comprises an amine solvent.

6. The process of any one of claims 1-5, wherein the purified natural gas stream comprises CO_2 in an amount of less than about 50 ppmv.

7. The process of any one of claims 1-6, wherein the purified natural gas stream comprises CO_2 in an amount of about 40 ppmv or less.

8. The process of any one of claims 1-7, wherein the purified natural gas stream comprises CO_2 in an amount of about 30 ppmv or less.

9. The process of any one of claims 1-8, wherein the purified natural gas stream comprises CO_2 in an amount of about 23 mole % or less.

10. The process of any one of claims 1-9, wherein the purified natural gas stream comprises H_2S in an amount of less than about 50 ppmv.

11. The process of any one of claims 1-10, wherein the purified natural gas stream comprises H_2S in an amount of 10 ppmv or less.

12. The process of any one of claims 1-11, wherein the purified natural gas stream comprises H_2S in an amount of 5 ppmv or less.

13. The process of any one of claims 1-12, wherein the purified natural gas stream comprises H_2S in an amount of 0 ppmv.

14. The process of any one of claims 1-13, wherein the process results in a loss of methane in an amount of about 7% or less.

15. The process of any one of claims 1-14, wherein the process results in a loss of methane in an amount of about 5 mole % or less.

16. The process of any one of claims 1-15, wherein the process results in a loss of methane in an amount of about 3 mole % or less.

17. The process of any one of claims 1-16, wherein the process results in a loss of methane in an amount of about 2 mole % or less.

18. The process of any one of claims 1-17, wherein the process results in a loss of methane in an amount of about 1 mole % or less.

19. The process of any one of claims 5-18, wherein each of the plurality of PTFE hollow fiber membranes maintains its stability in an amine solvent for at least 18 months.

20. The process of any one of claims 5-19, wherein each of the plurality of PTFE hollow fiber membranes maintains its stability in an amine solvent for at least 24 months.

21. The process of any one of claims 3-20, wherein each of the plurality of PTFE hollow fiber membranes maintains its stability in high temperatures of up to 150 degrees Celsius.

22. The process of any one of claims 3-21, wherein each of the plurality of PTFE hollow fiber membranes exhibits improved stability in an absorption system and desorption system.

23. The process of any one of claims 5-22, wherein the process results in a reduced amine solvent equipment footprint in comparison with conventional amine systems.

24. The process of any one of claims 1-23, wherein the process results in a decrease in capital expenditures in comparison to conventional amine systems.

25. The process of any one of claims 1-24, wherein the offshore platform comprises a fixed offshore platform.

26. The process of claim 25, wherein the fixed offshore platform comprises a pipeline.

27. The process of any one of claims 1-24, wherein the offshore platform comprises a floating offshore platform.

28. The process of claim 27, wherein the floating offshore platform comprises a floating liquefied natural gas (FLNG) system.

29. The process of claim 28, wherein the FLNG system comprises a ship or barge.

30. A hybrid gas-liquid contact system for an offshore platform, wherein the hybrid gas-liquid contact system comprises:

a membrane contactor and a solvent;

wherein the membrane contactor comprises a hydrophobic membrane module.

31. The hybrid gas-liquid contact system of claim 30, wherein the hydrophobic membrane module comprises a plurality of hollow fiber microporous membranes.

32. The hybrid gas-liquid contact system of claim 31, wherein each of the plurality of hollow fiber membranes comprises polytetrafluoroethylene (PTFE).

33. The hybrid gas-liquid contact system of any one of claims 30-32, wherein the solvent is selected from the group consisting of water, sea water, brackish water, an amine solvent or a combination of one or more thereof.

34. The hybrid gas-liquid contact system of any one of claims 30-33, wherein the solvent comprises an amine solvent.

35. The hybrid gas-liquid contact system of any one of claims 30-34, wherein the hybrid gas-liquid contact system reduces a carbon dioxide (CO_2) content in a natural gas stream to less than about 50 ppmv.

36. The hybrid gas-liquid contact system of claim 35, wherein the hybrid gas-liquid contact system reduces the CO_2 content in the natural gas stream to about 40 ppmv or less.

37. The hybrid gas-liquid contact system of claim 35 or 36, wherein the hybrid gas-liquid contact system reduces the CO_2 content in the natural gas stream to about 30 ppmv or less.

38. The hybrid gas-liquid contact system of any one of claims 35-37, wherein the hybrid gas-liquid contact system reduces the CO_2 content in the natural gas stream to about 23 mole % or less.

39. The hybrid gas-liquid contact system of any one of claims 30-38, wherein the hybrid gas-liquid contact system reduces a H_2S content in a natural gas stream to less than about 50 ppmv.

40. The hybrid gas-liquid contact system of claim 39, wherein the hybrid gas-liquid contact system reduces the H_2S content in the natural gas stream to about 10 ppmv or less.

41. The hybrid gas-liquid contact system of claim 39 or 40, wherein the hybrid gas-liquid contact system reduces the H_2S content in the natural gas stream to about 5 ppmv or less.

42. The hybrid gas-liquid contact system of any one of claims 39-41, wherein the hybrid gas-liquid contact system reduces the H_2S content in the natural gas stream to about 0 ppmv.

43. The hybrid gas-liquid contact system of any one of claims 30-42, wherein the hybrid gas-liquid contact system provides a loss of methane in an amount of about 7 mole % or less.

44. The hybrid gas-liquid contact system of any one of claims 30-43, wherein the hybrid gas-liquid contact system provides a loss of methane in an amount of about 5 mole % or less.

45. The hybrid gas-liquid contact system of any one of claims 30-44, wherein the hybrid gas-liquid contact system provides a loss of methane in an amount of about 3 mole % or less.

46. The hybrid gas-liquid contact system of any one of claims 30-45, wherein the hybrid gas-liquid contact system provides a loss of methane in an amount of about 2 mole % or less.

47. The hybrid gas-liquid contact system of any one of claims 30-46, wherein the hybrid gas-liquid contact system provides a loss of methane in an amount of about 1 mole % or less.

48. The hybrid gas-liquid contact system of any one of claims 32-47, wherein each of the plurality of PTFE hollow fiber membranes maintains its stability in an amine solvent for at least 18 months.

49. The hybrid gas-liquid contact system of any one of claims 32-48, wherein each of the plurality of PTFE hollow fiber membranes maintains its stability in an amine solvent for at least 24 months.

50. The hybrid gas-liquid contact system of any one of claims 32-49, wherein each of the plurality of PTFE hollow fiber membranes maintains its stability in high temperatures of up to 150 degrees Celsius.

51. The hybrid gas-liquid contact system of any one of claims 32-49, wherein each of the plurality of PTFE hollow fiber membranes exhibits improved stability in an absorption system and desorption system.

52. The hybrid gas-liquid contact system of any one of claims 34-35, wherein the hybrid gas-liquid contact system provides a reduced amine solvent equipment footprint in comparison with conventional amine systems.

53. The hybrid gas-liquid contact system of any one of claims 30-52, wherein the hybrid gas-liquid contact system provides a decrease in capital expenditures in comparison to conventional amine systems.

54. The hybrid gas-liquid contact system of any one of claims 30-53, wherein the offshore platform comprises a fixed offshore platform.

55. The hybrid gas-liquid contact system of claim 54, wherein the fixed offshore platform comprises a pipeline.

56. The hybrid gas-liquid contact system of any one of claims 54, wherein the offshore platform comprises a floating offshore platform.

57. The hybrid gas-liquid contact system of claim 56, wherein the floating offshore platform comprises a floating liquefied natural gas (FLNG) system.

58. The hybrid gas-liquid contact system of claim 57, wherein the FLNG system comprises a ship or barge.

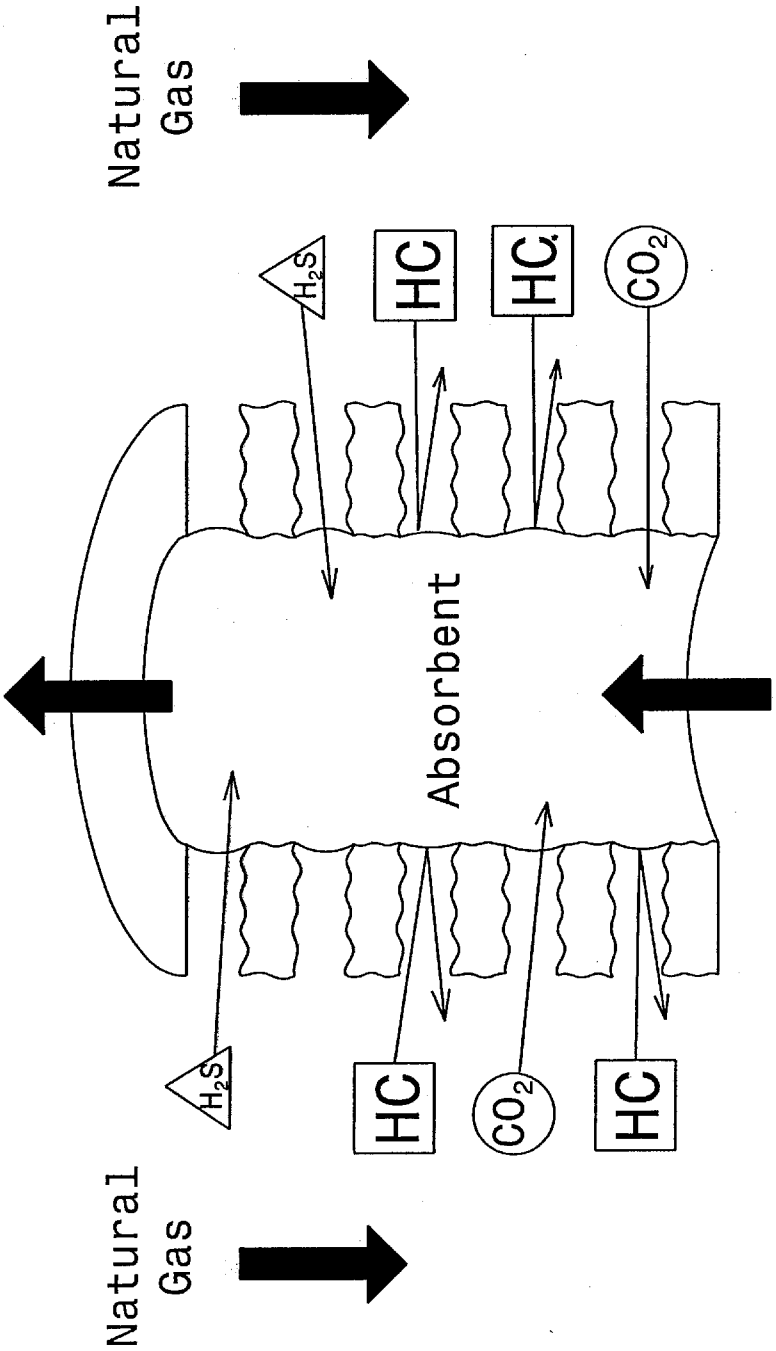

Fig. 1A

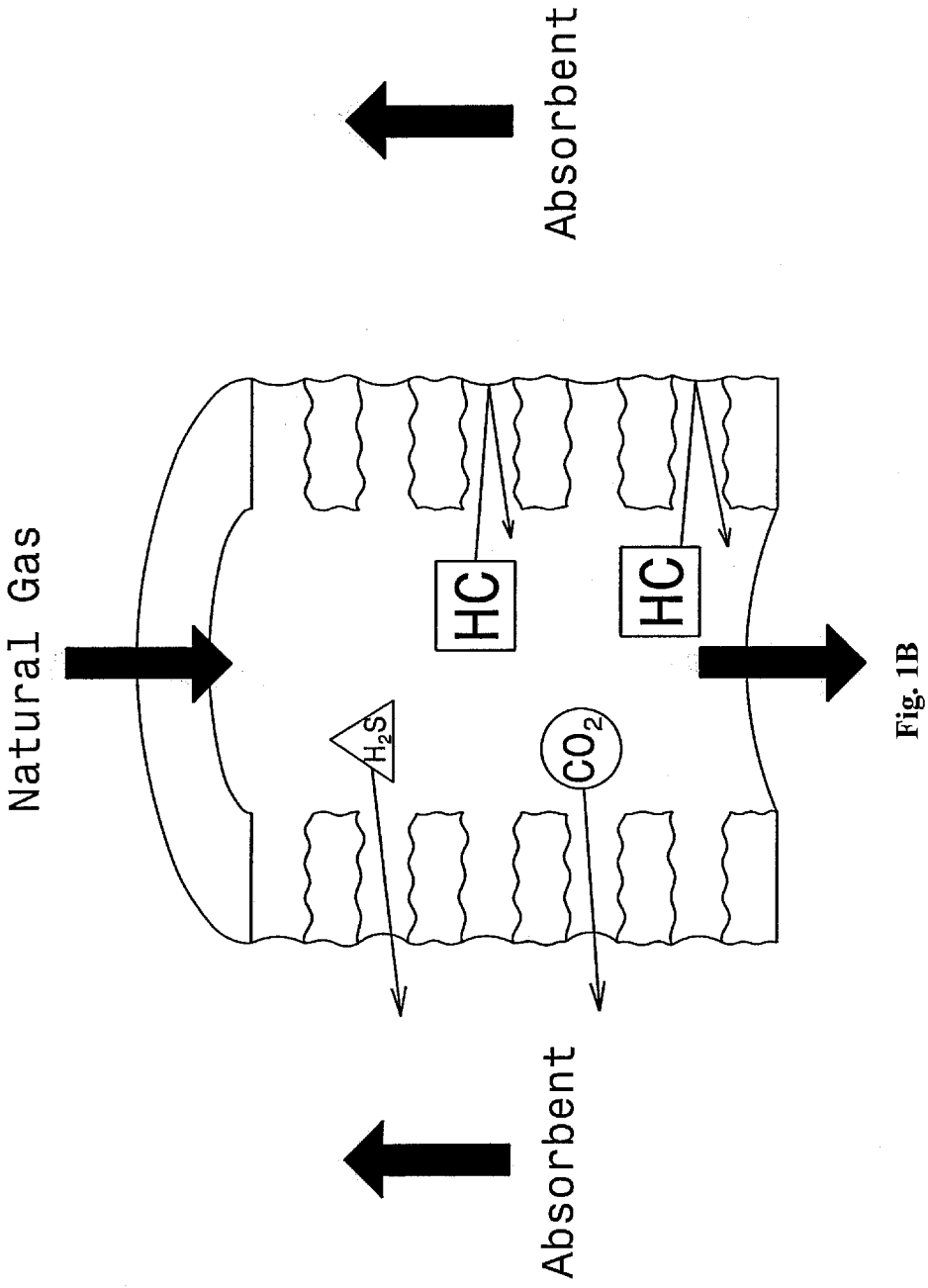

Fig. 1B

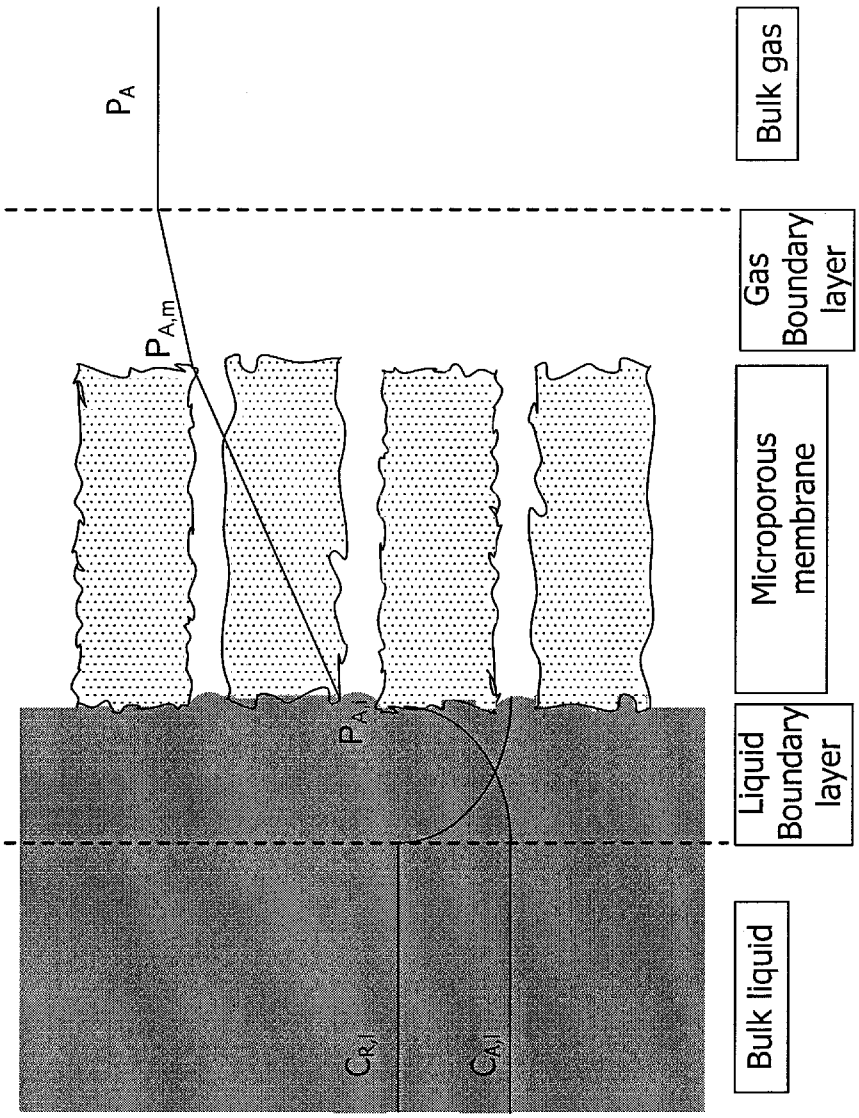
Bulk gas
Gas Boundary layer
Microporous membrane
Liquid Boundary layer
Bulk liquid
P_A
$P_{A,m}$
$P_{A,l}$
$C_{R,l}$
$C_{A,l}$

Fig. 2A

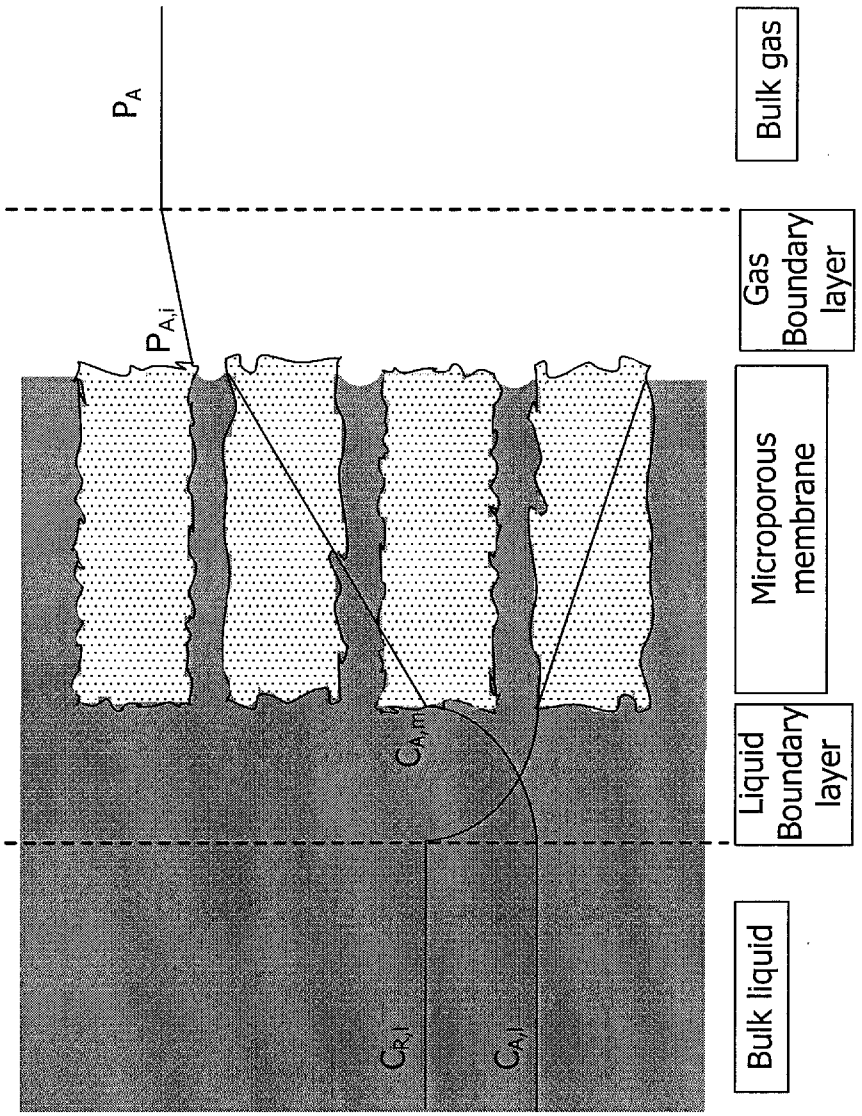
Bulk gas
Gas Boundary layer
Microporous membrane
Liquid Boundary layer
Bulk liquid
P_A
$P_{A,i}$
$C_{A,m}$
$C_{R,l}$
$C_{A,l}$

Fig. 2B

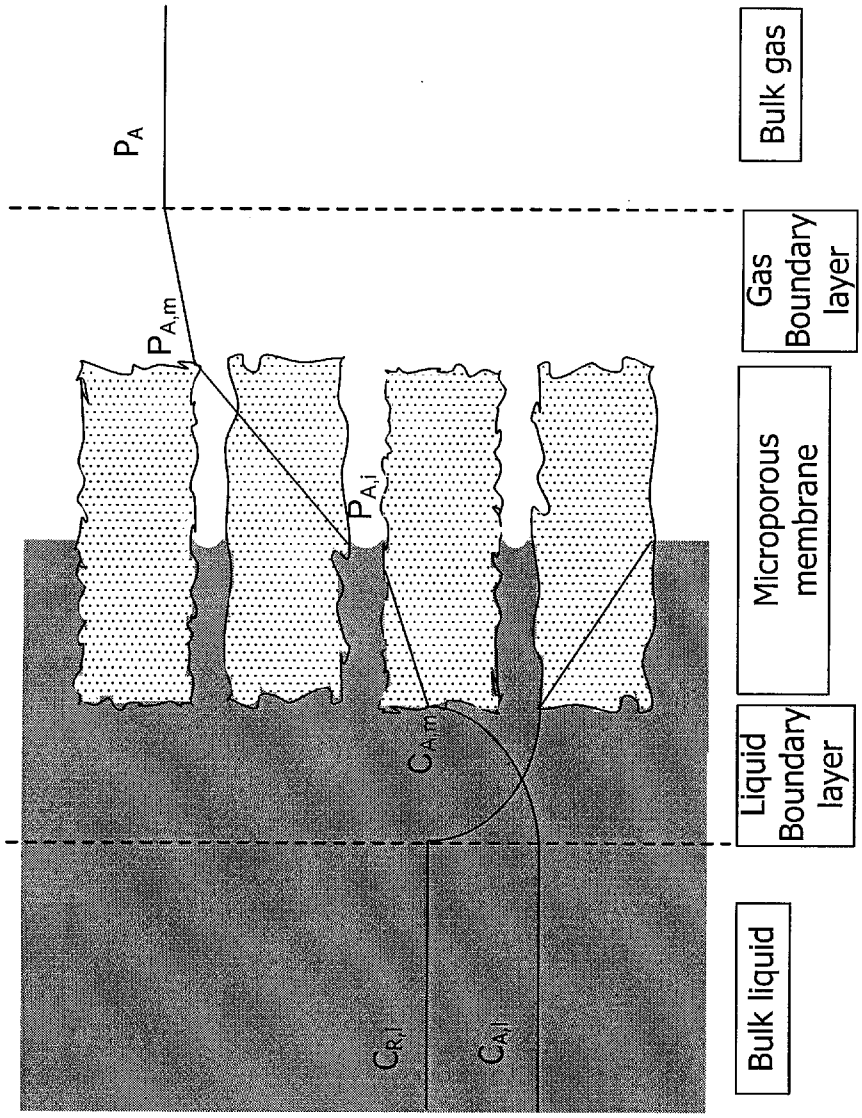
P_A
$P_{A,m}$
$P_{A,i}$
$C_{A,m}$
$C_{R,l}$
$C_{A,l}$
Bulk gas
Gas Boundary layer
Microporous membrane
Liquid Boundary layer
Bulk liquid

Fig. 2C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/TH2014/000022

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 53/22 (2015.01)
CPC - B01D 2053/224 (2015.04)
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)
IPC(8) - B01D 53/22, 53/62 (2015.01)
CPC - B01D 53/229, 53/62, 2053/224 (2015.04) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 95/51; 96/4 (keyword delimited)

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

Orbit, Google Scholar
Search terms used: natural gas, offshore, membrane, carbon dioxide, solvent, hydrophobic, polytetrafluoroethylene, amine, hollow fiber

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0058016 A1 (BANSAL) 08 March 2012 (08.03.2012) entire document	1-4, 30-33
A	US 8,388,732 B2 (DOONG et al) 05 March 2013 (05.03.2013) entire document	1-4, 30-33
A	US 2011/0290110 A1 (ZHOU et al) 01 December 2011 (01.12.2011) entire document	1-4, 30-33
A	US 2012/0247327 A1 (OMOLE) 04 October 2012 (04.10.2012) entire document	1-4, 30-33
X, P	US 2014/0309471 A1 (ZHOU et al) 16 October 2014 (16.10.2014) entire document	1-4, 30-33

☐ Further documents are listed in the continuation of Box C. ☐

* 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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 April 2015	30 APR 2015
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/TH2014/000022

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-29, 34-58
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.