SEPARATING CARBON DIOXIDE FROM NATURAL GAS LIQUIDS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application 61/711,130 filed October 8, 2012 entitled SEPARATING CARBON DIOXIDE FROM NATURAL GAS LIQUIDS, the entirety of which is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] Exemplary embodiments of the present techniques are directed to the separation of carbon dioxide (CO_2) from natural gas liquids (NGLs). More specifically, exemplary embodiments of the present techniques are directed to the separation of CO_2 from a hydrocarbon stream containing NGLs by cooling the hydrocarbon stream below the freezing point of CO_2 and removing the resulting CO_2 solids from the hydrocarbon stream.

BACKGROUND

[0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present techniques. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present techniques. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of prior art.

[0004] Natural gas reservoirs may often contain high levels of acid gases, such as carbon dioxide (CO_2). In these cases, a cryogenic process may provide an efficacious way to separate the acid gases from the methane. The cryogenic process could include a simple bulk fractionation, a Ryan-Holmes process, or a more complex cryogenic fractionation process. The cryogenic processes separate methane from CO_2 by condensation and fractionation, and can produce the acid gas in a liquid phase for efficient disposal via pumping. However, in the cryogenic processes, hydrocarbons heavier than methane, *e.g.*, natural gas liquids (NGLs), are separated with the CO_2 in a single liquid stream. Often, the CO_2 will be immediately reinjected for disposal.

[0005] In some locations, a natural gas reservoir contains high levels of CO_2. In such locations, it may be desirable to use a cryogenic process to separate the CO_2 from the methane. The cryogenic process could be a simple bulk fractionation process, a Ryan-Holmes process, or a Controlled Freeze Zone (CFZ™) process. These processes separate

[0068] In some embodiments, the azeotropic mixture **504** is flowed back into the system **400** upstream of the heat exchanger **414**. The azeotropic mixture **504** may be combined with the liquid stream **412** exiting the separation system **408**, and may be used to aid in the cooling of the liquid stream **412** prior to entry into the heat exchanger **414**. This may reduce the heat duty of the heat exchanger **414**, resulting in cost savings.

[0069] The block diagram of **Fig. 5** is not intended to indicate that the system **400** is to include all the components shown in **Fig. 5**. Further, any number of additional components not shown in **Fig. 5** may be included within the system **500**.

[0070] **Fig. 6** is a process flow diagram of a system **600** that can be used to separate CO_2 **602** from NGLs **604** using a COBC **606**. A hydrocarbon feed stream **608** may be flowed into the system **600** directly from one or more production wells, or from a dehydration unit, for example. The hydrocarbon feed stream **608** may include methane **610**, ethane and heavier hydrocarbons, CO_2 **602**, H_2S and other acid gases, and any other residual contaminants.

[0071] The hydrocarbon feed stream **608** may be injected into a cryogenic fractionation column **612**. The cryogenic fractionation column **612** may be a CFZ column or a Ryan-Holmes column, for example. The cryogenic fractionation column **612** may separate the methane **610** from the ethane and heavier hydrocarbons, CO_2 **602**, and other components within the hydrocarbon feed stream **608**.

[0072] The methane **610** may be flowed out of the cryogenic distillation column **612** as an overhead stream **614**. The overhead stream **614** may also include other low boiling point or non-condensable gases, such as nitrogen and helium. The overhead stream **614** may be flowed through a condenser **616**, which may condense the overhead stream **614**, producing a cooled methane stream **617**. The cooled methane stream **617** may then be flowed into a reflux drum **618**. From the reflux drum **618** a portion of the cooled methane stream **616** may be flowed out of the system **600** as a methane stream **610**, and the remaining portion of the cooled methane stream **617** may be reinjected into the cryogenic fractionation column **612** as a reflux stream **620** to aid in the separation process.

[0073] The ethane and heavier hydrocarbons, CO_2 **602**, and other components within the hydrocarbon feed stream **608** may be flowed out of the cryogenic fractionation column **612** as a bottoms stream **622**. The bottoms stream **622** may then be heated within a reboiler **624**, and a portion of the heated bottoms stream **622** may be returned to the cryogenic fractionation column **612** to provide heating. The remaining portion of the heated bottoms stream **622** may be a liquid stream **626** from which separate ethane and CO_2 streams are to be generated.

[0074] The liquid stream **626** may be flowed into a heat exchanger **628**. The heat exchanger **628** may be a shell-and-tube heat exchanger, a brazed aluminum heat exchanger, a double pipe heat exchanger, or a chiller bundle heat exchanger, among others. The heat exchanger **628** may pre-cool the liquid stream via indirect heat exchange with a cooling fluid **630**. In some embodiments, the heat exchanger **628** cools the liquid stream **626** to a temperature that is slightly above the freezing point of CO_2.

[0075] The resulting high-temperature liquid stream **632** may be flowed through a pressure reducing device **634**. The pressure reducing device **634** may be any type of device or valve that is capable of decreasing the pressure of the high-temperature liquid stream **632**, producing a low-pressure liquid stream **636**.

[0076] The low-pressure liquid stream **636** may be flowed into the COBC **606**. The COBC **606** may radially cool the high-temperature liquid stream **636** to a temperature that is below the freezing point of the CO_2 **602** via indirect heat exchange with a cooling fluid **640**. Further, the COBC **606** may use vibrations to prevent the CO2 solids from freezing on the sides, agglomerating, or plugging the COBC **606**. The COBC **606** provides a multiphase stream **644** including CO_2 solids and NGLs.

[0077] The multiphase stream **644** may be flowed into a solid-liquid separation system **644**. The solid-liquid separation system **644** may be a cyclonic separator or a separation column, among others. The solid-liquid separation system **644** may remove the CO_2 solids from the NGLs. The CO_2 **602** may be flowed out of the solid-liquid separation system **644** via a bottoms line **646**, and the NGLs **604** may be flowed out of the solid-liquid separation system **644** via an overhead line **648**. In addition, H_2S or other acid gases within the multiphase stream **644** may be flowed out of the overhead line **648** along with the NGLs **604**.

[0078] The process flow diagram of **Fig. 6** is not intended to indicate that the system **600** is to include all the components shown in **Fig. 6**. Further, any number of additional components not shown in **Fig. 6** may be included within the system **600**. For example, the system **600** may include a recirculation system, as discussed further with respect to **Fig. 6**.

[0079] **Fig. 7** is a process flow diagram of the system **600** of **Fig. 6** with the addition of a recirculation system for increasing the degree of separation of the CO_2 **602** and the NGLs **604**. Like numbered items are as described with respect to **Fig. 6**. The recirculation system may be useful for instances in which the proportion of CO_2 in the low-pressure liquid stream **636** is high. In such instances, the COBC **606** may not be able to crystallize all of the CO_2 in the low-pressure liquid stream **636** in one pass. Therefore, it may be desirable to reduce the

addition, the radial mixing of the liquid stream **802** may prevent the CO_2 solids from adhering to the baffles **814** or the walls of the circuitous COBC **800**.

[0086] The liquid stream **802** including the CO_2 solids may be flowed out of the inner tube **804** of the circuitous COBC **800** as a multiphase stream **816**. In addition, the warmed cooling fluid **808** may be flowed out of the outer tube **810** of the circuitous COBC **800**, and may be cooled and recycled to the circuitous COBC **800**.

[0087] The multiphase stream **816** may be flowed into a solid-liquid separation system **818**, which may remove the CO_2 solids from the NGLs within the multiphase stream **814**. In various embodiments, the solid-liquid separation system **818** is a cyclonic separation, as discussed further with respect to Fig .10.

[0088] **Fig. 9** is a schematic of a vertical COBC **900** that can be used to form CO_2 solids. Like numbered items are as described with respect to **Fig. 8**. The vertical COBC **900** may be similar to the circuitous COBC **800** discussed with respect to Fig .8. However, as shown in **Fig. 9**, the vertical COBC **900** may include a single vertical structure, rather than a circuitous structure.

[0089] Further, in various embodiments, the pump **812** of the vertical COBC **900** may be replaced with a thermoacoustic generator. The thermoacoustic generator may produce a pulsating flow of the liquid stream **802** using a resonant frequency in the COBC **900**. In addition, the thermoacoustic generator may aid in the cooling of the liquid stream **802**.

[0090] **Fig. 10** is a schematic of a cyclonic separation **1000** that can used to separate CO_2 **1002** from NGLs **1004**. The cyclonic separation**1000** may be any of the solid-liquid separation systems **426**, **644**, or **818** discussed with respect to **Figs. 4-9**. The cyclonic separation system **1000** may include a cyclonic separator **1006** and a separation vessel **1008**.

[0091] A multiphase stream **1010** may be flowed into the cyclonic separator **1006** from an oscillatory crystallization unit **1012**. The oscillatory crystallization unit **1012** may be the oscillatory crystallization unit **422** discussed with respect to **Figs. 4** and **5**, the circuitous COBC **800** discussed with respect to **Fig. 6**, or the vertical COBC discussed with respect to **Fig. 7**. The multiphase stream **1010** may include CO_2 solids **1014** and NGLs.

[0092] As the multiphase stream **1010** enters the cyclonic separator **1006**, the location of the inlet line within the cyclonic separator **1006** may impart a radial acceleration and a tangential velocity component to the multiphase stream **1010**. A swirl element may be added to impart a further radial acceleration through the rotation of twisted swirl vanes. The swirl vanes may be arranged parallel or in series on the swirl element. The tangential velocity of the multiphase stream **1010** may cause the CO_2 solids **1014**, which are heavier and denser

SEPARATING CARBON DIOXIDE FROM NATURAL GAS LIQUIDS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is the National Stage of International Application No. PCT/US2013/062686, filed September 30, 2013, which claims the benefit of U.S. Provisional Patent Application 61/711,130 filed October 8, 2012 entitled SEPARATING CARBON DIOXIDE FROM NATURAL GAS LIQUIDS, the entirety of which is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] Exemplary embodiments of the present techniques are directed to the separation of carbon dioxide (CO_2) from natural gas liquids (NGLs). More specifically, exemplary embodiments of the present techniques are directed to the separation of CO_2 from a hydrocarbon stream containing NGLs by cooling the hydrocarbon stream below the freezing point of CO_2 and removing the resulting CO_2 solids from the hydrocarbon stream.

BACKGROUND

[0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present techniques. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present techniques. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of prior art.

[0004] Natural gas reservoirs may often contain high levels of acid gases, such as carbon dioxide (CO_2). In these cases, a cryogenic process may provide an efficacious way to separate the acid gases from the methane. The cryogenic process could include a simple bulk fractionation, a Ryan-Holmes process, or a more complex cryogenic fractionation process. The cryogenic processes separate methane from CO_2 by condensation and fractionation, and can produce the acid gas in a liquid phase for efficient disposal via pumping. However, in the cryogenic processes, hydrocarbons heavier than methane, *e.g.*, natural gas liquids (NGLs), are separated with the CO_2 in a single liquid stream. Often, the CO_2 will be immediately reinjected for disposal.

[0005] In some locations, a natural gas reservoir contains high levels of CO_2. In such locations, it may be desirable to use a cryogenic process to separate the CO_2 from the methane. The cryogenic process could be a simple bulk fractionation process, a Ryan-Holmes process, or a Controlled Freeze Zone (CFZ™) process. These processes separate

[0068] In some embodiments, the azeotropic mixture **504** is flowed back into the system **400** upstream of the heat exchanger **414**. The azeotropic mixture **504** may be combined with the liquid stream **412** exiting the separation system **408**, and may be used to aid in the cooling of the liquid stream **412** prior to entry into the heat exchanger **414**. This may reduce the heat duty of the heat exchanger **414**, resulting in cost savings.

[0069] The block diagram of **Fig. 5** is not intended to indicate that the system **400** is to include all the components shown in **Fig. 5**. Further, any number of additional components not shown in **Fig. 5** may be included within the system **500**.

[0070] **Fig. 6** is a process flow diagram of a system **600** that can be used to separate CO_2 **602** from NGLs **604** using a COBC **606**. A hydrocarbon feed stream **608** may be flowed into the system **600** directly from one or more production wells, or from a dehydration unit, for example. The hydrocarbon feed stream **608** may include methane **610**, ethane and heavier hydrocarbons, CO_2 **602**, H_2S and other acid gases, and any other residual contaminants.

[0071] The hydrocarbon feed stream **608** may be injected into a cryogenic fractionation column **612**. The cryogenic fractionation column **612** may be a CFZ column or a Ryan-Holmes column, for example. The cryogenic fractionation column **612** may separate the methane **610** from the ethane and heavier hydrocarbons, CO_2 **602**, and other components within the hydrocarbon feed stream **608**.

[0072] The methane **610** may be flowed out of the cryogenic fractionation column **612** as an overhead stream **614**. The overhead stream **614** may also include other low boiling point or non-condensable gases, such as nitrogen and helium. The overhead stream **614** may be flowed through a condenser **616**, which may condense the overhead stream **614**, producing a cooled methane stream **617**. The cooled methane stream **617** may then be flowed into a reflux drum **618**. From the reflux drum **618** a portion of the cooled methane stream **617** may be flowed out of the system **600** as a methane stream **610**, and the remaining portion of the cooled methane stream **617** may be reinjected into the cryogenic fractionation column **612** as a reflux stream **620** to aid in the separation process.

[0073] The ethane and heavier hydrocarbons, CO_2 **602**, and other components within the hydrocarbon feed stream **608** may be flowed out of the cryogenic fractionation column **612** as a bottoms stream **622**. The bottoms stream **622** may then be heated within a reboiler **624**, and a portion of the heated bottoms stream **622** may be returned to the cryogenic fractionation column **612** to provide heating. The remaining portion of the heated bottoms stream **622** may be a liquid stream **626** from which separate ethane and CO_2 streams are to be generated.

[0074] The liquid stream **626** may be flowed into a heat exchanger **628**. The heat exchanger **628** may be a shell-and-tube heat exchanger, a brazed aluminum heat exchanger, a double pipe heat exchanger, or a chiller bundle heat exchanger, among others. The heat exchanger **628** may pre-cool the liquid stream via indirect heat exchange with a cooling fluid **630**. In some embodiments, the heat exchanger **628** cools the liquid stream **626** to a temperature that is slightly above the freezing point of CO_2.

[0075] The resulting high-temperature liquid stream **632** may be flowed through a pressure reducing device **634**. The pressure reducing device **634** may be any type of device or valve that is capable of decreasing the pressure of the high-temperature liquid stream **632**, producing a low-pressure liquid stream **636**.

[0076] The low-pressure liquid stream **636** may be flowed into the COBC **606**. The COBC **606** may radially cool the high-temperature liquid stream **632** to a temperature that is below the freezing point of the CO_2 **602** via indirect heat exchange with a cooling fluid **640**. Further, the COBC **606** may use vibrations to prevent the CO_2 solids from freezing on the sides, agglomerating, or plugging the COBC **606**. The COBC **606** provides a multiphase stream **642** including CO_2 solids and NGLs.

[0077] The multiphase stream **642** may be flowed into a solid-liquid separation system **644**. The solid-liquid separation system **644** may be a cyclonic separator or a separation column, among others. The solid-liquid separation system **644** may remove the CO_2 solids from the NGLs. The CO_2 **602** may be flowed out of the solid-liquid separation system **644** via a bottoms line **646**, and the NGLs **604** may be flowed out of the solid-liquid separation system **644** via an overhead line **648**. In addition, H_2S or other acid gases within the multiphase stream **642** may be flowed out of the overhead line **648** along with the NGLs **604**.

[0078] The process flow diagram of **Fig. 6** is not intended to indicate that the system **600** is to include all the components shown in **Fig. 6**. Further, any number of additional components not shown in **Fig. 6** may be included within the system **600**. For example, the system **600** may include a recirculation system, as discussed further with respect to **Fig. 6**.

[0079] **Fig. 7** is a process flow diagram of the system **600** of **Fig. 6** with the addition of a recirculation system for increasing the degree of separation of the CO_2 **602** and the NGLs **604**. Like numbered items are as described with respect to **Fig. 6**. The recirculation system may be useful for instances in which the proportion of CO_2 in the low-pressure liquid stream **636** is high. In such instances, the COBC **606** may not be able to crystallize all of the CO_2 in the low-pressure liquid stream **636** in one pass. Therefore, it may be desirable to reduce the

addition, the radial mixing of the liquid stream **802** may prevent the CO_2 solids from adhering to the baffles **814** or the walls of the circuitous COBC **800**.

[0086] The liquid stream **802** including the CO_2 solids may be flowed out of the inner tube **804** of the circuitous COBC **800** as a multiphase stream **816**. In addition, the warmed cooling fluid **808** may be flowed out of the outer tube **810** of the circuitous COBC **800**, and may be cooled and recycled to the circuitous COBC **800**.

[0087] The multiphase stream **816** may be flowed into a solid-liquid separation system **818**, which may remove the CO_2 solids from the NGLs within the multiphase stream **816**. In various embodiments, the solid-liquid separation system **818** is a cyclonic separation, as discussed further with respect to Fig .10.

[0088] **Fig. 9** is a schematic of a vertical COBC **900** that can be used to form CO_2 solids. Like numbered items are as described with respect to **Fig. 8**. The vertical COBC **900** may be similar to the circuitous COBC **800** discussed with respect to Fig .8. However, as shown in **Fig. 9**, the vertical COBC **900** may include a single vertical structure, rather than a circuitous structure.

[0089] Further, in various embodiments, the pump **812** of the vertical COBC **900** may be replaced with a thermoacoustic generator. The thermoacoustic generator may produce a pulsating flow of the liquid stream **802** using a resonant frequency in the COBC **900**. In addition, the thermoacoustic generator may aid in the cooling of the liquid stream **802**.

[0090] **Fig. 10** is a schematic of a cyclonic separation **1000** that can used to separate CO_2 **1002** from NGLs **1004**. The cyclonic separation**1000** may be any of the solid-liquid separation systems **426**, **644**, or **818** discussed with respect to **Figs. 4-9**. The cyclonic separation system **1000** may include a cyclonic separator **1006** and a separation vessel **1008**.

[0091] A multiphase stream **1010** may be flowed into the cyclonic separator **1006** from an oscillatory crystallization unit **1012**. The oscillatory crystallization unit **1012** may be the oscillatory crystallization unit **422** discussed with respect to **Figs. 4** and **5**, the circuitous COBC **800** discussed with respect to **Fig. 6**, or the vertical COBC discussed with respect to **Fig. 7**. The multiphase stream **1010** may include CO_2 solids **1014** and NGLs.

[0092] As the multiphase stream **1010** enters the cyclonic separator **1006**, the location of the inlet line within the cyclonic separator **1006** may impart a radial acceleration and a tangential velocity component to the multiphase stream **1010**. A swirl element may be added to impart a further radial acceleration through the rotation of twisted swirl vanes. The swirl vanes may be arranged parallel or in series on the swirl element. The tangential velocity of the multiphase stream **1010** may cause the CO_2 solids **1014**, which are heavier and denser