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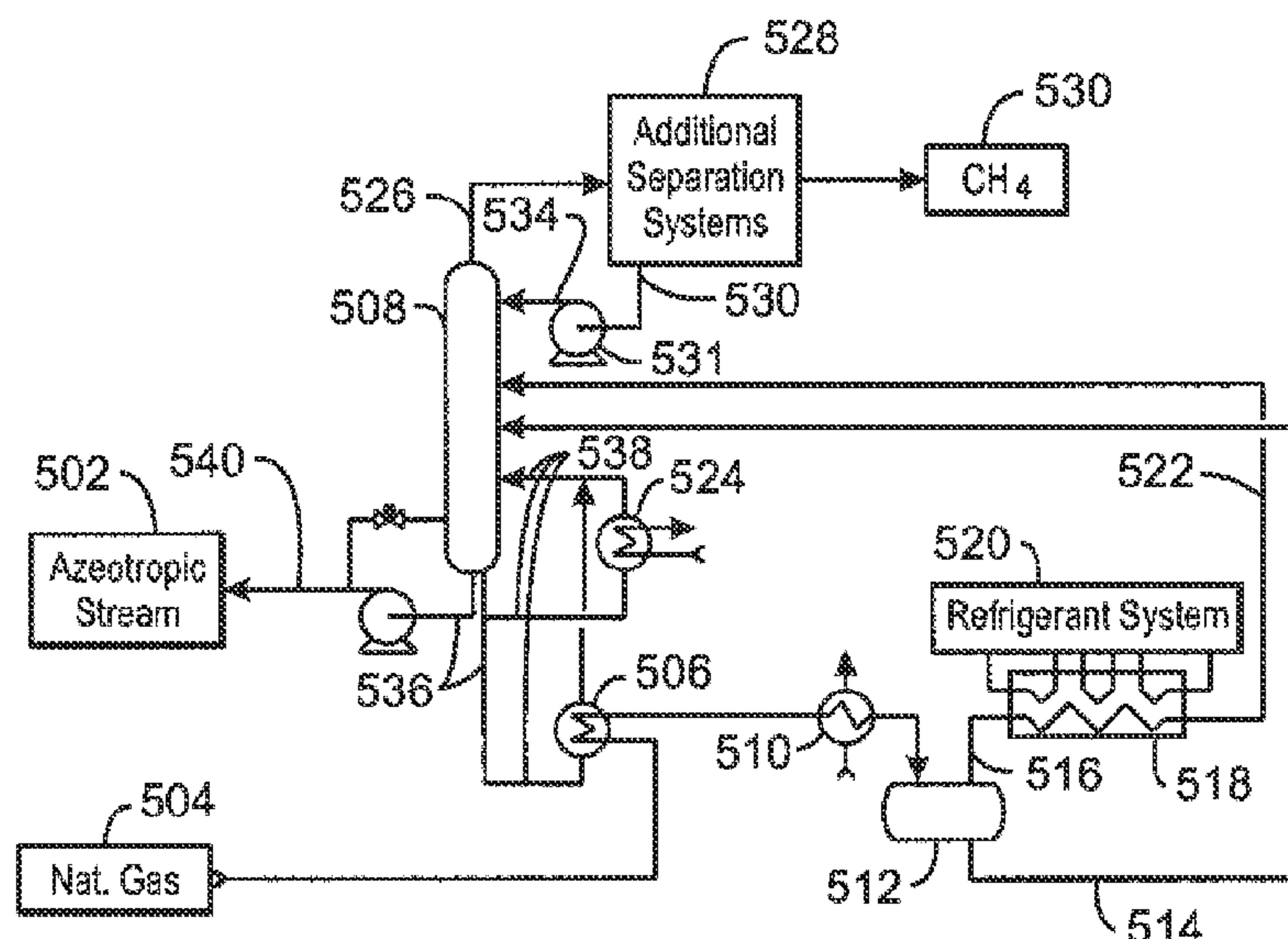
(71) Demandeur/Applicant:
EXXONMOBIL UPSTREAM RESEARCH COMPANY,
US

(72) Inventeur/Inventor:
OELFKE, RUSSELL H., US

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : SEPARATION DE DIOXYDE DE CARBONE ET D'ETHANE PRESENTS DANS UN COURANT MELANGE

(54) Title: SEPARATING CARBON DIOXIDE AND ETHANE FROM A MIXED STREAM



500
FIG. 5

(57) **Abrégé/Abstract:**

Embodiments described herein provide methods and systems for separating a mixed ethane and CO₂. A method described includes generating a liquid stream including ethane and CO₂. The liquid stream is flashed to form an ethane vapor stream and solid CO₂. The solid CO₂ is accumulated in an accumulation vessel and the gas is removed from the top of the accumulation vessel.

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(71) Applicant (for all designated States except US): **EXXON-MOBIL UPSTREAM RESEARCH COMPANY** [US/US]; CORP-URC-SW 359, P.O. Box 2189, Houston, TX 77252-2189 (US).

(72) Inventor; and

(71) Applicant (for US only): **OELFKE, Russell, H.** [US/US]; 18215 Spruce Greek Drive, Houston, TX 77084 (US).

(74) Agents: **TIMMINS, Stephen** et al.; Exxonmobil Upstream Research Company, Corp-urc-sw359, P.O. Box 2189, Houston, TX 77252-2189 (US).

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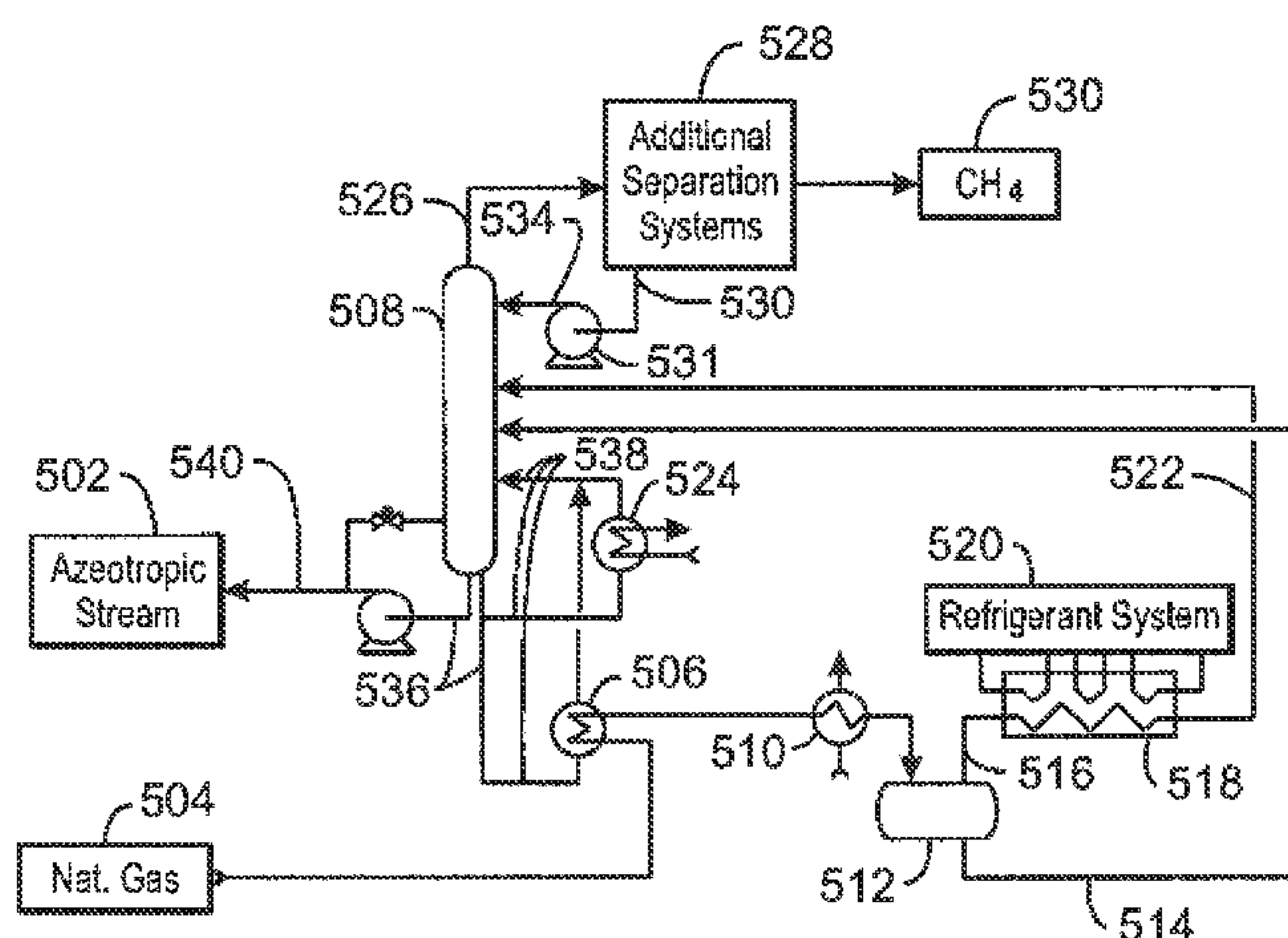
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[Continued on next page]

(54) Title: SEPARATING CARBON DIOXIDE AND ETHANE FROM A MIXED STREAM



(57) Abstract: Embodiments described herein provide methods and systems for separating a mixed ethane and CO₂. A method described includes generating a liquid stream including ethane and CO₂. The liquid stream is flashed to form an ethane vapor stream and solid CO₂. The solid CO₂ is accumulated in an accumulation vessel and the gas is removed from the top of the accumulation vessel.

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FIG. 5

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SEPARATING CARBON DIOXIDE AND ETHANE FROM A MIXED STREAM**CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of U.S. Provisional Patent Application 61/613,606 filed March 21, 2012 entitled SEPARATING CARBON DIOXIDE AND
5 ETHANE FROM A MIXED STREAM, the entirety of which is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present application is directed to the separation of carbon dioxide from ethane, wherein the liquid acid gas stream is composed primarily of hydrogen sulphide and
10 carbon dioxide.

BACKGROUND

[0003] Natural gas reservoirs may often contain high levels of acid gases, such as CO₂. 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-
15 Holmes process, or a more complex cryogenic fractionation process. The cryogenic processes separate methane from CO₂ by condensation and fractionation, and can produce the acid gas in a liquid phase for efficient disposal via pumping. However, in the cryogenic processes heavier hydrocarbons are separated with the CO₂ in a single liquid stream. Often, the CO₂ will be immediately reinjected for disposal, where the mixture will not cause any
20 problems.

[0004] In some locations, a natural gas reservoir contains high levels of CO₂. It is advantageous in these cases to use a cryogenic process to separate the CO₂ from the methane. The cryogenic process could be simple bulk fractionation, a Ryan-Holmes, or a Controlled Freeze Zone (CFZ™) process. These processes separate methane from CO₂ by condensation
25 / fractionation, and can provide the CO₂ as a liquid for efficient disposal. However, in these processes all hydrocarbons heavier than methane (C₂+ or “ethane plus”) are also condensed and separated with the CO₂. Normally, the CO₂ will be reinjected for disposal, but the hydrocarbons are valuable and it is preferred that they be recovered for sale.

[0005] Separation of the heavier hydrocarbons can be performed by fractionation.
30 However, ethane forms an azeotropic mixture with CO₂, as discussed with respect to Fig. 1. The azeotropic prevents separation by normal techniques.

[0006] **Fig. 1** is a temperature - composition phase plot **100** showing the equilibrium concentrations of CO₂ in a mixture with ethane at 4,137 kilopascals (kPa, 600 psia). The x-axis **102** indicates the mole fraction of CO₂, while the y-axis **104** represents the temperature in degrees Celsius (°C). The concentration of the CO₂ in the vapor phase **106** matches the concentration of the CO₂ in the liquid phase **108** at about 70% CO₂ / 30% ethane, as indicated by an arrow **110**. This prevents separation-by-fractionation across the azeotrope (left to right, or right to left).

[0007] **Fig. 2** is a temperature - composition phase plot **200** showing the equilibrium concentrations of CO₂ in a mixture with ethane at 689.5 kPa (100 psia). Like numbered items are as described with respect to **Fig. 1**. As this plot **200** shows, concentration of the CO₂ in the vapor phase **106** approaches the concentration of the CO₂ in the liquid phase **108** at about 60% CO₂ / 40% ethane, as indicated by an arrow **202**. This prevents separation-by-fractionation across the azeotrope (left to right, or right to left). As these plots **100** and **200** indicate, complete separation by fractionation cannot be achieved without some additional separation processes.

[0008] Since the vapor and liquid compositions are equal at some point (70% CO₂ at 4,137 kPa and 60% CO₂ at 689.5 kPa), complete separation by fractionation cannot be achieved without some additional factor. Current practice for CO₂ / ethane separation includes various methods. For example, a heavy component (lean oil) can be added, which preferentially absorbs the ethane. This is called “extractive distillation.” As another example, two-pressure fractionation can be used to exploit the small difference in the azeotropic composition between different pressures, for example, using two fractionators to fractionate at both 4,137 kPa and 689.5 kPa. This requires very large recycle stream, large fractionation systems, and is very energy intensive. Methods to exploit other physical and chemical properties (not dependent on vapor-liquid equilibria) can be used in conjunction with fractionation to achieve separation. These methods may include the use of amines in a chemical reaction with CO₂, gas permeation membranes, or molecular sieves.

[0009] For example, U.S. Patent No. 4,246,015, to Styring, discloses a method for separating carbon dioxide and ethane based on washing ethane from frozen carbon dioxide. The separation is accomplished by freezing the carbon dioxide in a carbon dioxide and ethane mixture and washing the ethane from the solid carbon dioxide with a liquid hydrocarbon having at least three carbon atoms. The freezing process may be preceded by distillation of a carbon dioxide-ethane mixture to form an azeotropic mixture. A subsequent distillation may

be used to separate the wash hydrocarbon from the carbon dioxide. In addition, if desired, the ethane-wash hydrocarbon mixture may be similarly separated in a subsequent distillation stage.

[0010] U.S. Patent Application Publication No. 2002/0189443, by McGuire, discloses a method of removing carbon dioxide or hydrogen sulfide from a high pressure mixture with methane. The high pressure gas is expanded through a flow channel having a convergent section followed by a divergent section with an intervening throat which functions as an aerodynamic expander. The flow channel is operated at temperatures low enough to result in the formation of solid carbon dioxide and solid hydrogen sulfide particles, which increases the efficiency of carbon dioxide and hydrogen sulfide removal.

[0011] International Patent Publication No. WO/2008/095258, by Hart, discloses a method for decreasing the concentration on carbon dioxide in a natural gas feed stream containing ethane and C₃+ hydrocarbons. The process involves cooling the natural gas feed stream under a first set of conditions to produce a liquid stream of carbon dioxide, ethane and C₃+ hydrocarbons and a gas stream having a reduced carbon dioxide concentration. The liquid stream is separated from the gas stream, and C₃+ hydrocarbons may be separated from the liquid stream. The gas stream is then cooled under a second set of conditions to produce a sweetened natural gas stream and a second liquid containing liquid carbon dioxide and/or carbon dioxide solids. The sweetened natural gas stream is separated from the second liquid.

[0012] International Patent Publication No. WO/2008/084945, by Prast, discloses a method and assembly for removing and solidifying carbon dioxide from a fluid stream. The assembly has a cyclonic fluid separator with a tubular throat portion arranged between a converging fluid inlet section and a diverging fluid outlet section and a swirl creating device. The separation vessel has a tubular section positioned on and in connection with a collecting tank. A fluid stream with carbon dioxide is injected into the separation assembly. A swirling motion is imparted to the fluid stream so as to induce outward movement. The swirling fluid stream is then expanded such that components of carbon dioxide in a meta-stable state within the fluid stream are formed. Subsequently, the outward fluid stream with the components of carbon dioxide is extracted from the cyclonic fluid separator and provided as a mixture to the separation vessel. The mixture is then guided through the tubular section towards the collecting tank, while providing processing conditions such that solid carbon dioxide is formed. Finally, solidified carbon dioxide is extracted.

[0013] Each of these methods presents a drawback. For example, using a lean oil contaminates the ethane, and requires large amounts of heat, for regenerating the lean oil. Further, large lean oil circulation rates are needed and the technique does not allow complete ethane recovery. Two-pressure fractionation systems require very large recycle streams and equipment sizes, increasing costs. Techniques that use amines, membranes, and mole sieves all release the CO₂ as a vapor at low pressure, increasing the cost of disposal. Finally, the expander separation devices generate the CO₂ as a solid. Thus, there is a need for a better method of separating CO₂ and ethane.

SUMMARY

10 [0014] An embodiment described herein provides a method for separating a mixed ethane and CO₂ stream. The method includes generating a liquid stream comprising ethane and CO₂ and passing the liquid stream through a flash valve into an accumulation vessel, forming a gas that is enhanced in ethane, and forming solid CO₂. The solid CO₂ is accumulated in the accumulation vessel, and the gas is removed from the top of the accumulation vessel.

15 [0015] Another embodiment provides a system for separating a mixed stream of CO₂ and ethane. The system includes a flash valve configured to isoenthalpically flash the mixed stream forming solid CO₂ and a vapor stream enhanced in ethane, and an accumulation vessel configured to capture the solid CO₂.

20 [0016] Another embodiment provides a method for purifying a natural gas stream. The method includes dehydrating the natural gas stream and cryogenically separating the natural gas stream into a methane rich fraction, a natural gas liquids fraction, and an azeotropic stream in a cryogenic purification system. The azeotropic stream is flashed to form solid CO₂ and an ethane enriched vapor stream. The solid CO₂ is removed from the ethane enriched vapor stream in an accumulation vessel and the ethane enriched vapor stream is purified to form a liquid ethane product.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:

30 [0018] **Fig. 1** is a temperature - composition phase plot showing the equilibrium concentrations of CO₂ in a mixture with ethane at 4,137 kPa;

[0019] **Fig. 2** is a temperature - composition phase plot showing the equilibrium concentrations of CO₂ in a mixture with ethane at 689.5 kPa;

[0020] Fig. 3 is a plot of the freezing conditions used to form solid CO₂ in a mixture with a hydrocarbon;

[0021] Fig. 4 is a block diagram of a system that can be used to separate CO₂ and ethane as part of a natural gas purification process ;

5 [0022] Fig. 5 is a simplified process flow diagram of a cryogenic separation system that can be used to generate an azeotropic stream;

[0023] Fig. 6 is a simplified process diagram of a separation system for separating CO₂ from an azeotropic mixture with ethane; and

[0024] Fig. 7 is a block diagram of a method for generating a CO₂ product stream and an
10 ethane stream from an azeotropic stream using a flashing process.

DETAILED DESCRIPTION

[0025] In the following detailed description section, specific embodiments of the present techniques are described. However, to the extent that the following description is specific to a particular embodiment or a particular use of the present techniques, this is intended to be
15 for exemplary purposes only and simply provides a description of the exemplary embodiments. Accordingly, the techniques are not limited to the specific embodiments described below, but rather, include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

[0026] At the outset, for ease of reference, certain terms used in this application and their
20 meanings as used in this context are set forth. To the extent a term used herein is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Further, the present techniques are not limited by the usage of the terms shown below, as all equivalents, synonyms, new developments, and terms or techniques that serve the same or a similar
25 purpose are considered to be within the scope of the present claims.

[0027] “Acid gases” are contaminants that are often encountered in natural gas streams. Typically, these gases include carbon dioxide (CO₂) and hydrogen sulfide (H₂S), although any number of other contaminants may also form acids. Acid gases are commonly removed by contacting the gas stream with an absorbent, such as an amine, which may react with the
30 acid gas. When the absorbent becomes acid-gas “rich,” a desorption step can be used to separate the acid gases from the absorbent. The “lean” absorbent is then typically recycled for further absorption. As used herein a “liquid acid gas stream” is a stream of acid gases that

are condensed into the liquid phase, for example, including CO₂ dissolved in H₂S and vice-versa.

[0028] An “azeotrope” or “azeotropic mixture” is a system of two or more components in which the liquid composition and vapor composition are equal at a certain pressure and
5 temperature. In practice, this means that the components of an azeotropic mixture are constant-boiling at that pressure and temperature and generally cannot be separated during a phase change.

[0029] As used herein, a “column” is a separation vessel in which a counter current flow is used to isolate materials on the basis of differing properties. In an absorbent column, a
10 physical solvent is injected into the top, while a mixture of gases to be separated is flowed through the bottom. As the gases flow upwards through the falling stream of absorbent, one gas species is preferentially absorbed, lowering its concentration in the vapor stream exiting the top of the column. In a fractionation column, liquid and vapor phases are counter-
currently contacted to effect separation of a fluid mixture based on boiling points or vapor
15 pressure differences. The high vapor pressure, or lower boiling, component will tend to concentrate in the vapor phase whereas the low vapor pressure, or higher boiling, component will tend to concentrate in the liquid phase.

[0030] “Cold box” refers to an insulated enclosure which encompasses sets of process equipment such as heat exchangers, columns, and phase separators. Such sets of process
20 equipment may form the whole or part of a given process.

[0031] “Compressor” refers to a device for compressing a working gas, including gas-vapor mixtures or exhaust gases. Compressors can include pumps, compressor turbines, reciprocating compressors, piston compressors, rotary vane or screw compressors, and devices and combinations capable of compressing a working gas.

25 [0032] “Cryogenic distillation” has been used to separate carbon dioxide from methane since the relative volatility between methane and carbon dioxide is reasonably high. The overhead vapor is enriched with methane and the bottoms product is enriched with carbon dioxide and other heavier hydrocarbons. Cryogenic distillation processing requires the proper combination of pressure and temperature to achieve the desired product recovery.

30 [0033] The term “gas” is used interchangeably with “vapor,” and means a substance or mixture of substances in the gaseous state as distinguished from the liquid or solid state. Likewise, the term “liquid” means a substance or mixture of substances in the liquid state as

distinguished from the gas or solid state.

[0034] “Heat exchanger” refers to any equipment arrangement adapted to allow the passage of heat energy from one or more streams to other streams. The heat exchange may be either direct (e.g., with the streams in direct contact) or indirect (e.g. with the streams
5 separated by a mechanical barrier). The streams exchanging heat energy may be one or more lines of refrigerant, heating, or cooling utilities, one or more feed streams, or one or more product streams. Examples include a shell-and-tube heat exchanger, a cryogenic spool-wound heat exchanger, or a brazed aluminum-plate fin type, among others.

[0035] A “hydrocarbon” is an organic compound that primarily includes the elements
10 hydrogen and carbon, although nitrogen, sulfur, oxygen, metals, or any number of other elements may be present in small amounts. As used herein, hydrocarbons generally refer to organic materials that are harvested from hydrocarbon containing sub-surface rock layers, termed reservoirs. For example, natural gas is normally composed primarily of the hydrocarbon methane.

15 [0036] The term “natural gas” refers to a multi-component gas obtained from a crude oil well (associated gas) or from a subterranean gas-bearing formation (non-associated gas). The composition and pressure of natural gas can vary significantly. A typical natural gas stream contains methane (C_1) as a significant component. Raw natural gas will also typically contain ethane (C_2), higher molecular weight hydrocarbons, one or more acid gases (such as
20 carbon dioxide, hydrogen sulfide, carbonyl sulfide, carbon disulfide, and mercaptans), and minor amounts of contaminants such as water, helium, nitrogen, iron sulfide, wax, and crude oil.

[0037] “Pressure” is the force exerted per unit area by the gas on the walls of the volume. Pressure can be shown as pounds per square inch (psi). “Atmospheric pressure” refers to the
25 local pressure of the air. “Absolute pressure” (psia) refers to the sum of the atmospheric pressure (14.7 psia at standard conditions) plus the gauge pressure (psig). “Gauge pressure” (psig) refers to the pressure measured by a gauge, which indicates only the pressure exceeding the local atmospheric pressure (i.e., a gauge pressure of 0 psig corresponds to an absolute pressure of 14.7 psia). The term “vapor pressure” has the usual thermodynamic
30 meaning. For a pure component in an enclosed system at a given pressure, the component vapor pressure is essentially equal to the total pressure in the system.

[0038] A “separation vessel” is a vessel wherein an incoming feed is separated into individual vapor and liquid fractions. A separation vessel may include a flash drum in which a stream is flashed to form vapor and liquid components. The vapor component is removed from an upper outlet, while the liquid component is removed from a lower outlet.

- 5 [0039] “Substantial” when used in reference to a quantity or amount of a material, or a specific characteristic thereof, refers to an amount that is sufficient to provide an effect that the material or characteristic was intended to provide. The exact degree of deviation allowable may in some cases depend on the specific context.

Overview

- 10 [0040] Methods and systems described herein use the heat of vaporization of ethane to freeze entrained CO₂ to a solid form, allowing a substantially complete separation of the components. The process works by taking a liquid mixture of CO₂ and ethane, chilling it as much as possible without forming solid CO₂, and, then, reducing the mixture's pressure by flashing it into a solids-accumulation vessel. The pressure of the flash is selected to vaporize
15 all the ethane by heat liberated from the freezing CO₂ (heat of fusion). Solid CO₂ deposits in the vessel, while the vapor stream, now enriched in ethane above the azeotrope, can be distilled by using conventional fractionation for partial ethane recovery. The distillation overhead stream (at the azeotropic composition again) is chilled and recycled back to the feed, as liquid CO₂ / Ethane. The process may be further understood with respect to **Fig. 3**.

- 20 [0041] **Fig. 3** is a plot **300** of the freezing conditions used to form solid CO₂ in a mixture with a hydrocarbon. In the plot **300**, the x-axis **302** represents the temperature of the mixture in degrees Fahrenheit, while the y-axis **304** represents the CO₂ content of the liquid phase in mol %. The line **306** on the plot **300** represents a division between a first region **308** in which solid CO₂ forms, and a second region **310** in which solid CO₂ does not form. At temperatures
25 of about – 62 °C, solid CO₂ forms from a 70% / 30%: CO₂ / ethane mixture as shown at point **312** in the plot **300**. Ethane, however, does not freeze, but will be either a vapor or liquid, depending on the pressure, temperature, and residual CO₂ level. The solid will be nearly pure CO₂, resulting in a separation.

- [0042] **Fig. 4** is a block diagram of a system **400** that can be used to isolate a CO₂ product
30 stream **402** as part of a natural gas purification process. The purified natural gas **404** may, for example, be used to power an electrical generation system **406**. The system **400** is not limited to the blocks shown, but may include any number of configurations, including, for

example, providing a purified natural gas stream **404** to other customers through a commercial pipeline.

[0043] In the system **400**, one or more production wells **407** can be used to produce a raw natural gas stream **408**. The raw natural gas stream **408** may include a substantial amount of carbon dioxide, ethane, and other components. In some embodiments, the raw natural gas stream **408** may have a low-BTU content, e.g., between about 500 and 950 BTUs per standard cubic foot.

[0044] The raw natural gas stream **408** can be fed to a dehydration unit **410** in which water vapor may be removed using glycol dehydration, desiccants, or a Pressure Swing Adsorption (PSA) unit, among other processes. The dehydration unit **410** is not limited to the arrangement shown, but may be included at any number of points in the system **400**, or eliminated if not needed. Generally, dehydration is used to prepare the natural gas for cryogenic separation by removing water, which could freeze and plug the systems.

[0045] The dehydrated stream **412** may be fed to a purification system **414**, which may use any number of processes to remove contaminants, including natural gas liquids (NGL) **416**, carbon dioxide, and other acid gases. The purification system **414** may include a cryogenic distillation unit, for example, using a Ryan-Holmes process. Other cryogenic distillation techniques may be used, such as the controlled freeze zone (CFZTM) technology available from Exxon Mobil. Both of these cryogenic processes can generate an azeotropic stream **418** that includes ethane and CO₂, as well as other compounds. In various embodiments, any number of other techniques that generate a liquid acid gas stream may also be used for purification, such as a warm gas processing system. In addition to removing the azeotropic stream **418**, the purification system **414** may also remove at least a portion of the higher carbon number hydrocarbons, e.g., C₂ and higher, for example, by fractionation. The higher carbon number hydrocarbons may be combined to form a NGL stream **416**, among others, which may also be marketed as a product. However, as discussed above, the formation of the azeotrope will cause a portion of ethane will remain in the azeotropic stream **418** as a mixture with the CO₂.

[0046] The azeotropic stream **418** from the purification may be further processed to generate the CO₂ stream **402**, which may be used for enhanced oil recovery, commercial sales, or other purposes. The processing is performed in a separation system **420** that flashes the azeotropic stream **418** to generate an ethane stream **422**, which can be combined back into the natural gas liquids **416** or added to the gas stream **404**.

[0047] After purification, the gas stream **404** may be a mixture of methane and various inert gases, such as nitrogen and helium, and may include the ethane stream **422**. This gas stream **404** can be directly used, for example, as a low BTU natural gas stream to power an electric power generation system **406**. Other operations, such as the separation of a helium enriched stream, may also be performed prior to the usage. An electrical generation plant **406** may provide other, higher value, products for sale, including electrical power **424** to a power grid, heat **426** for other processes, or both. In some embodiments, the electrical generation plant **406** may purchase the gas stream **404** from a pipeline associated with the producer. The techniques described herein are not limited to electric power generation using low BTU streams, but may be used with any purification process in which the separation of ethane from carbon dioxide may be useful.

[0048] The system **400** described herein has a number of advantages over current technologies. For example, it produces a liquid carbon dioxide stream for easy injection, while producing a clean vapor ethane stream for sale. Further, the system **400** integrates heat demands and cooling sources to decrease the need for external refrigeration in the separation system **420**. The process is based on solidifying the CO₂ and flashing the ethane. Since the azeotropic stream **418** is in the liquid phase, the vaporization of the azeotropic stream **418** can be used to drive the process, with the heat of vaporization of the ethane cooling the CO₂, and the heat of solidification from the CO₂ driving the vaporization of the ethane. Additional cooling or heating may be provided to balance the energy transfer.

[0049] The purification system **414** can include any number of processes that produce a liquid acid gas stream, including, for example, the Ryan-Holmes process, a bulk fractionation process, or a controlled freeze zone plant. The separation system **420** can be retrofitted onto an existing purification system **414** to have all or part of the liquid acid gas stream produced by these processes re-directed to the separation system **420** to extract higher value ethane from CO₂ mixtures. One example of a cryogenic separation process that may be used is shown in **Fig. 5**.

Cryogenic separation forming a liquid acid gas stream

[0050] **Fig. 5** is a simplified process flow diagram of a cryogenic separation system **500** that can be used to generate an azeotropic stream **502**. In the separation system **500**, a natural gas stream **504** can be cooled by providing some of the heat used by the process, for example, by being passed through a heat exchanger **506** to provide heat for reboiler service on a cryogenic fractionation column **508**. The natural gas stream **504** can be further chilled in

another heat exchanger **510**, and then flashed into a flash drum **512**. The bottoms stream **514** from the flash drum **512** can be sent into the cryogenic fractionation column **508**. The vapor stream **516** from the overhead of the flash drum **512** can be further cooled in a cold box **518**, for example, by exchanging heat with a number of refrigerant systems **520**, such as high pressure, mid-pressure, and low pressure propane chillers. The resulting stream **522** is injected into the cryogenic fractionation column **508**. In addition to heating from the heat exchanger **506** on the natural gas feed stream **504**, a reboiler heat exchanger **524** may provide additional heating or cooling to the cryogenic fractionation column **508**.

[0051] The overhead stream **526** from the cryogenic fractionation column **508** will include the methane from the natural gas feed **504**, as well as other low boiling point or non-condensable gases, such as nitrogen and helium. Additional separation systems **528**, including columns, cold boxes, and the like, may be used to generate a CH₄ product stream **530** at a chosen purity level. A portion **530** of the overhead stream **526** may be fed to a pump **531** to be reinjected into the cryogenic fractionation column **508** as a reflux stream **534**.

[0052] The bottoms stream **536** from the cryogenic fractionation column **508** can be separated into two streams. A reboiler stream **538** is heated and returned to the cryogenic fractionation column **508** to provide heating. An outlet stream **540** is removed from the bottoms stream **536** for disposal. In embodiments, this outlet stream **540** forms the azeotropic stream **502** used for the generation of the separated ethane and CO₂ streams, as described with respect to Fig. 6.

Separation of CO₂ from an azeotropic stream

[0053] Fig. 6 is a simplified process diagram of a separation system **600** for separating CO₂ from an azeotropic mixture with ethane. Tables 1 and 2 provide details of a simulation example of the process. The numbers in the diamonds in Fig. 6 correspond to the like numbered columns in Table 1, which show the properties and compositions of the labeled point. The separation system **600** shown in Fig. 6 has a number of advantages over conventional technology. For example, the ethane and CO₂ can be substantially separated, with minimal residual contamination or hydrocarbon loss. The CO₂ stream **602** is recovered as a pressurized liquid, allowing it to be pumped to disposal pressure. This facilitates EOR or geo-sequestration at minimum power. The ethane stream **604** is recovered as a chilled liquid, and can be either heated and revaporized to provide refrigeration for the process, or processed to a liquid ethane product by further chilling.

[0054] The separation system **600** can be substantially heat-integrated, minimizing external heat or power requirements. A separation of a methane stream **606** from the ethane stream **604** is performed at the same time as the separation of ethane and CO₂. This separation eliminates a need for an additional demethanizer downstream. The methane stream **606** is returned to the CFZ or bulk fractionation column, for example, being combined with the natural gas stream **504** discussed with respect to Fig. 5.

[0055] The separation system **600** begins when the azeotropic stream **502** is blended with a liquids stream **608** from a methane separator **610**. The mixing element **611** can be a static mixer, or merely a pipe joint coupling the two streams **502** and **608**. In this example, the CO₂ content of the azeotropic stream **502** is about 70%, which is very close to the azeotropic composition at 4,137 kPa (600 psia). In embodiments in which the CO₂ content is lower, the azeotropic stream **502** can be directed to the ethane fractionator **612**, e.g., mixed with the fractionator feed stream **614**, to remove as much ethane as possible by conventional fractionation, prior to solid CO₂ formation. In embodiments in which the CO₂ content of the azeotropic stream **502** is greater than 70%, another fractionator could be included upstream of the separation system **600** to generate the azeotropic stream **502** as an overhead product by removing as much CO₂ as possible prior to using the subject technology. In both cases, the final concentration of the CO₂ and ethane in the azeotropic stream **502** after separation is limited by the azeotrope, e.g., to around 70% CO₂ and 30% ethane at 4,137 kPa (600 psia).

[0056] From the mixing element **611**, a combined feed stream **616** is passed through an isoenthalpic expansion element **618**, such as a Joule-Thompson valve. The expanded stream **620** is chilled as a result of the flashing, causing the CO₂ to solidify as the ethane and some CO₂ vaporizes. The expanded stream **620** is passed into one of two solid accumulation vessels **622** or **624**. In this example, the inlet valve **626** to and outlet valve **628** from the first solid accumulation vessel **630** are open, allowing the CO₂ solids to be captured in the vessel, while the ethane rich vapor stream **632** exits from the top of the vessel.

[0057] The ethane rich vapor stream **632** is compressed in a raw ethane compressor **634**. The compressed feed stream **636** is cooled in an ethane fractionator feed cooler **638** to form the fractionator feed stream **614**. The fractionator feed stream **614** is injected into a column **640** in the ethane fractionator **612**. A bottom stream **642** from the column **640** is heated in a reboiler **644**, before being returned to the column **640** as a heated stream **646**. A portion of the bottom stream **642** is taken from the reboiler **644** as the ethane stream **604**.

[0058] The overhead stream **648** from the column **640** is sent to a reflux condenser and reflux accumulator tank **650**. A liquid stream is taken from the bottom of the reflux accumulator tank **650** and injected into the top of the column **640** as a reflux stream **652**. The vapor stream from the top of reflux accumulator tank **650** is removed as a CO₂ / ethane recycle stream **654**. The CO₂ / ethane recycle stream **654** is chilled in a recycle condenser **656**, forming a liquid recycle stream **658**. The liquid recycle stream **658** is flashed in the methane separator **610**. As discussed, the liquid stream **608** from the methane separator **610** is combined with the azeotropic mixture **502**. The gas from the top of the methane separator **610** forms the methane stream **606**, which can be returned to the cryogenic separation process.

TABLE 1: Example Process Data

	1	2	3	4	5	7	8
Temperature - Deg C	-62	-91	-52	15	-62	-62	-62
Pressure - kPa	689.5	151.7	779.1	848.1	689.5	689.5	689.5
Flowrate (kgmole/hr)	453.7	614.8	313.3	313.3	161.1	614.8	185.3
Flowrate (k SM3/D)	257.7	349.0	177.9	177.9	91.4	349.0	105.2
Methane Mole Fraction	0.01000	0.01203	0.02362	0.02362	0.01776	0.01203	0.03995
Ethane Mole Fraction	0.30000	0.32877	0.64518	0.64518	0.40980	0.32877	0.40000
CO ₂ Mole Fraction	0.69000	0.65919	0.33121	0.33121	0.57243	0.65919	0.56005
	9	10	11	12	13	14	
Temperature - Deg C	-62	-55	-87	-87	8	-39	
Pressure - kPa	689.5	758.5	151.7	151.7	4240.4	792.9	
Flowrate (kgmole/hr)	24.2	185.3	313.3	301.5	301.5	128.1	
Flowrate (k SM3/D)	13.9	105.2	177.9	171.1	171.1	72.7	
Methane Mole Fraction	0.18739	0.03995	0.02362	0.00000	0.00000	0.00000	
Ethane Mole Fraction	0.33493	0.40000	0.64518	0.00000	0.00000	0.99978	
CO ₂ Mole Fraction	0.47768	0.56005	0.33121	1.00000	1.00000	0.00022	

[0059] During operations, the first solid accumulation vessel **622** fills with solid CO₂. When enough solid CO₂ has accumulated in the first solid accumulation vessel **630**, the flashing liquid can be sent to a second solid accumulation vessel **624** by opening the inlet valve **660** and outlet valve **662** on the second solid accumulation vessel **624** and closing the

inlet valve **626** to vessel **622**. The first solid accumulation vessel **622** can be heated by an internal heating coil **664**, sublimating some CO₂ to displace any remaining hydrocarbons. Once the hydrocarbons are displaced, the outlet valve **628** on the first solid accumulation vessel **622** can then be closed, allowing the pressure to rise until the CO₂ can melt, forming liquid CO₂. When the CO₂ has finished melting, the drainage valve **666** at the bottom of the first solid accumulation vessel **622** can be opened to allow the CO₂ stream **602** to be drained for sales or disposal. Once the second solid accumulation vessel **624** has a sufficient amount of CO₂, the process can be repeated. After hydrocarbons are purged, the vessel is isolated, and the CO₂ is melted, a drainage valve **668** can be opened to drain the CO₂ stream **602** from the second solid accumulation vessel **624**.

[0060] The energy balance of the process is shown in Table 2. The numbers in column 2 correspond to the circled numbers in Fig. 6. As can be seen from the values, the total heat released by the process is 2 MW, while the total heat adsorbed by the process is 2.21 MW, for a net heat input of 0.21 mW. At least a portion of that heat may be provided by cooling the initial natural gas feed **504** to the cryogenic separation process. In addition to the 352 kW used to power the raw ethane compressor **634**, other energy may be required to provide refrigeration make-up.

TABLE 2: Heat Balance

Heat Sources:	1	Recycle Condenser Q	595	kW
	2	Ethane Splitter Cond Q	595	kW
	3	Splitter Feed Cooler Q	811	kW
		TOTAL:	2	MW
Heat Sinks:	4	Ethane Splitter Reboiler Q	709	kW
	5	CO ₂ Sensible Heating Q	741	kW
	6	CO ₂ Heat of Fusion Q	762	kW
		TOTAL:	2.21	MW
Power Requirements:	7	Raw Ethane Compressor	352	kW

Method for separating CO₂ and ethane

[0061] Fig. 7 is a block diagram of a method **700** for generating a CO₂ product stream and an ethane stream from an azeotropic stream using a flashing process. The method **700** begins at block **702** with the separation of an azeotropic stream from a natural gas product. The azeotropic stream may be isolated using a cryogenic separation process as described with respect to Fig. 4. However, any separation process that generates an azeotropic stream may

be used. If the azeotropic stream is generated as a gas, a chilling and condensation step can be added to condense the gas prior to separation. At block 704, the azeotropic stream is flowed through a flash valve into a flash vessel to solidify CO₂ and flash ethane, as described with respect to Fig. 6. At block 706, the solidified CO₂ is allowed to accumulate in the flash vessel. At block 708, a determination is made as to whether the flash vessel is full. If so, at block 710, accumulation of the solid CO₂ is switched to an empty flash vessel that had been on standby. Process flow with the new flash vessel returns to block 704 to continue with the flashing, as indicated by an arrow 712.

[0062] The process continues for the full flash vessel at block 714, where heat is added to sublime a small portion of the CO₂, e.g., about less than about 5%, to release any trapped hydrocarbons. After the sublimation, at block 716, the vessel is blocked in and the temperature and pressure are allowed to rise until the CO₂ melts. The vessel is drained and the liquid CO₂ is provided as a product at block 718. The empty flash vessel is then placed in standby at block 720, and process flow for the empty vessel returns to block 710 to wait for the current accumulation vessel to fill, as indicated by an arrow 722.

[0063] The ethane that is flashed off to create the solid CO₂ at block 706 is combined with the sublimed CO₂ and hydrocarbon from block 714, as indicated by arrows 724. At block 726, the combined stream is compressed and chilled to form a raw liquid ethane stream. At block 728, the raw liquid ethane stream is stripped to remove a contaminated stream that contains methane and CO₂ from the ethane. The purified ethane stream is provided as a product at block 730. Methane is separated from the contaminated stream as a gas at block 732, and, at block 734. The remaining material, which includes ethane and CO₂, is returned to block 704 to be combined with the azeotropic stream for flashing in the flash vessel, as indicated by an arrow 736.

25 Embodiments

[0064] Embodiments as described herein may include any combinations of the elements in the following numbered paragraphs:

1. A method for separating a mixed ethane and CO₂ stream, including:
 - generating a liquid stream including ethane and CO₂;
 - 30 passing the liquid stream through a flash valve into an accumulation vessel, forming a gas that is enhanced in ethane, and forming solid CO₂;
 - accumulating the solid CO₂ in the accumulation vessel; and

removing the gas from the top of the accumulation vessel.

2. The method of paragraph 1, including cryogenically separating the liquid stream from a natural gas feed stream.

3. The method of paragraphs 1 or 2, including switching to a second
5 accumulation vessel when the accumulation vessel is substantially filled with solid CO₂.

4. The method of paragraph 3, including heating the solid CO₂ in the accumulation vessel to sublime a fraction of the CO₂, removing at least a portion of hydrocarbons trapped in the solid CO₂.

5. The method of paragraphs 1, 2, or 3, including
10 blocking in the accumulation vessel;
heating the accumulation vessel; and
and allowing the temperature and pressure to rise in the accumulation vessel until the CO₂ melts and forms liquid CO₂.

6. The method of paragraph 5, including:
15 draining the liquid CO₂ from the accumulation vessel; and
providing the liquid CO₂ as a product stream.

7. The method of any of paragraphs 1-3, or 5, including:
condensing the ethane stream;
stripping the ethane stream to remove a contaminated ethane stream that
20 includes methane and CO₂;
separating methane from the contaminated ethane stream; and
combining the contaminated ethane stream with the liquid stream.

8. The method of paragraph 7, including returning the methane to a separate purification unit.

25 9. The method of any of paragraphs 1-3, 5, or 7, including fractionating the liquid stream prior the flash valve to remove excess CO₂ and form an azeotropic mixture.

10. The method any of paragraphs 1-3, 5, 7, or 9, including fractionating the liquid stream prior to the flash valve to remove excess ethane and form an azeotropic mixture.

11. A system for separating a mixed stream of CO₂ and ethane, including:
a flash valve configured to isoenthalpically flash the mixed stream forming solid CO₂ and a vapor stream enhanced in ethane; and
an accumulation vessel configured to capture the solid CO₂.
- 5 12. The system of paragraph 11, including a cryogenic separation system configured to form the mixed stream from a natural gas feed.
13. The system of paragraphs 11 or 12, including a compressor and a chiller configured to recondense the vapor stream forming a raw ethane stream.
14. The system of paragraph 13, including a fractionator configured to separate a
10 contaminated ethane stream including ethane and CO₂ from the raw ethane stream.
15. The system of paragraph 14, wherein the fractionator is configured to isolate a liquid ethane product stream.
16. The system of paragraph 14, including a flash vessel configured to separate methane from the contaminated ethane stream.
- 15 17. The system of any of paragraphs 11-13, including a plurality of accumulation vessels, wherein each sequential accumulation vessel is configured to begin accumulating solid CO₂ when a previous accumulation vessel is substantially filled with CO₂.
18. The system of any of paragraphs 11-13, or 17, including a heater configured to warm solid CO₂ in the accumulation vessel and drive off trapped hydrocarbon.
- 20 19. The system of any of paragraphs 11-13, 17, or 18, wherein the accumulation vessel is configured to reach a temperature and pressure that allows the solid CO₂ to melt, forming a liquid CO₂ product stream.
20. The system of any of paragraphs 11-13, or 17-19, wherein the accumulation vessel is configured to form liquid CO₂ from the solid CO₂.
- 25 21. A method for purifying a natural gas stream including:
dehydrating the natural gas stream;
cryogenically separating the natural gas stream into a methane rich fraction, a natural gas liquids fraction, and an azeotropic stream in a cryogenic purification system;
30 flashing the azeotropic stream to form solid CO₂ and an ethane enriched vapor

stream;

removing the solid CO₂ from the ethane enriched vapor stream in an accumulation vessel; and

purifying the ethane enriched vapor stream to form a liquid ethane product.

5 22. The method of paragraph 21, including:

separating a recycle stream including CO₂, ethane, and methane from the ethane enriched vapor stream;

separating a methane stream from the recycle stream; and

returning the methane stream to the cryogenic purification system.

10 [0065] While the present techniques may be susceptible to various modifications and alternative forms, the exemplary embodiments discussed above have been shown only by way of example. However, it should again be understood that the techniques is not intended to be limited to the particular embodiments disclosed herein. Indeed, the present techniques include all alternatives, modifications, and equivalents falling within the true spirit and scope
15 of the appended claims.

CLAIMS

What is claimed is:

1. A method for separating a mixed ethane and CO₂ stream, comprising:
generating a liquid stream comprising ethane and CO₂;
5 passing the liquid stream through a flash valve into an accumulation vessel, forming a gas that is enhanced in ethane, and forming solid CO₂;
accumulating the solid CO₂ in the accumulation vessel; and
removing the gas from the top of the accumulation vessel.
2. The method of claim 1, comprising cryogenically separating the liquid stream from a
10 natural gas feed stream.
3. The method of claim 1, comprising switching to a second accumulation vessel when the accumulation vessel is substantially filled with solid CO₂.
4. The method of claim 3, comprising heating the solid CO₂ in the accumulation vessel to sublime a fraction of the CO₂, removing at least a portion of hydrocarbons trapped in the
15 solid CO₂.
5. The method of claim 1, comprising
blocking in the accumulation vessel;
heating the accumulation vessel; and
and allowing the temperature and pressure to rise in the accumulation vessel until the
20 CO₂ melts and forms liquid CO₂.
6. The method of claim 5, comprising:
draining the liquid CO₂ from the accumulation vessel; and
providing the liquid CO₂ as a product stream.
7. The method of claim 1, comprising:
25 condensing the ethane stream;
stripping the ethane stream to remove a contaminated ethane stream that includes methane and CO₂;

separating methane from the contaminated ethane stream; and

combining the contaminated ethane stream with the liquid stream.

8. The method of claim 7, comprising returning the methane to a separate purification unit.

5 9. The method of claim 1, comprising fractionating the liquid stream prior the flash valve to remove excess CO₂ and form an azeotropic mixture.

10. The method of claim 1, comprising fractionating the liquid stream prior to the flash valve to remove excess ethane and form an azeotropic mixture.

11. A system for separating a mixed stream of CO₂ and ethane, comprising:

10 a flash valve configured to isoenthalpically flash the mixed stream forming solid CO₂ and a vapor stream enhanced in ethane; and

an accumulation vessel configured to capture the solid CO₂.

12. The system of claim 11, comprising a cryogenic separation system configured to form the mixed stream from a natural gas feed.

15 13. The system of claim 11, comprising a compressor and a chiller configured to recondense the vapor stream forming a raw ethane stream.

14. The system of claim 13, comprising a fractionator configured to separate a contaminated ethane stream comprising ethane and CO₂ from the raw ethane stream.

15. The system of claim 14, wherein the fractionator is configured to isolate a liquid
20 ethane product stream.

16. The system of claim 14, comprising a flash vessel configured to separate methane from the contaminated ethane stream.

17. The system of claim 11, comprising a plurality of accumulation vessels, wherein each sequential accumulation vessel is configured to begin accumulating solid CO₂ when a
25 previous accumulation vessel is substantially filled with CO₂.

18. The system of claim 11, comprising a heater configured to warm solid CO₂ in the accumulation vessel and drive off trapped hydrocarbon.

19. The system of claim 11, wherein the accumulation vessel is configured to reach a temperature and pressure that allows the solid CO₂ to melt, forming a liquid CO₂ product
30 stream.

20. The system of claim 11, wherein the accumulation vessel is configured to form liquid CO₂ from the solid CO₂.
21. A method for purifying a natural gas stream comprising:
- dehydrating the natural gas stream;
- 5 cryogenically separating the natural gas stream into a methane rich fraction, a natural gas liquids fraction, and an azeotropic stream in a cryogenic purification system;
- flashing the azeotropic stream to form solid CO₂ and an ethane enriched vapor stream;
- removing the solid CO₂ from the ethane enriched vapor stream in an accumulation vessel; and
- 10 purifying the ethane enriched vapor stream to form a liquid ethane product.
22. The method of claim 21, comprising:
- separating a recycle stream comprising CO₂, ethane, and methane from the ethane enriched vapor stream;
- separating a methane stream from the recycle stream; and
- 15 returning the methane stream to the cryogenic purification system.

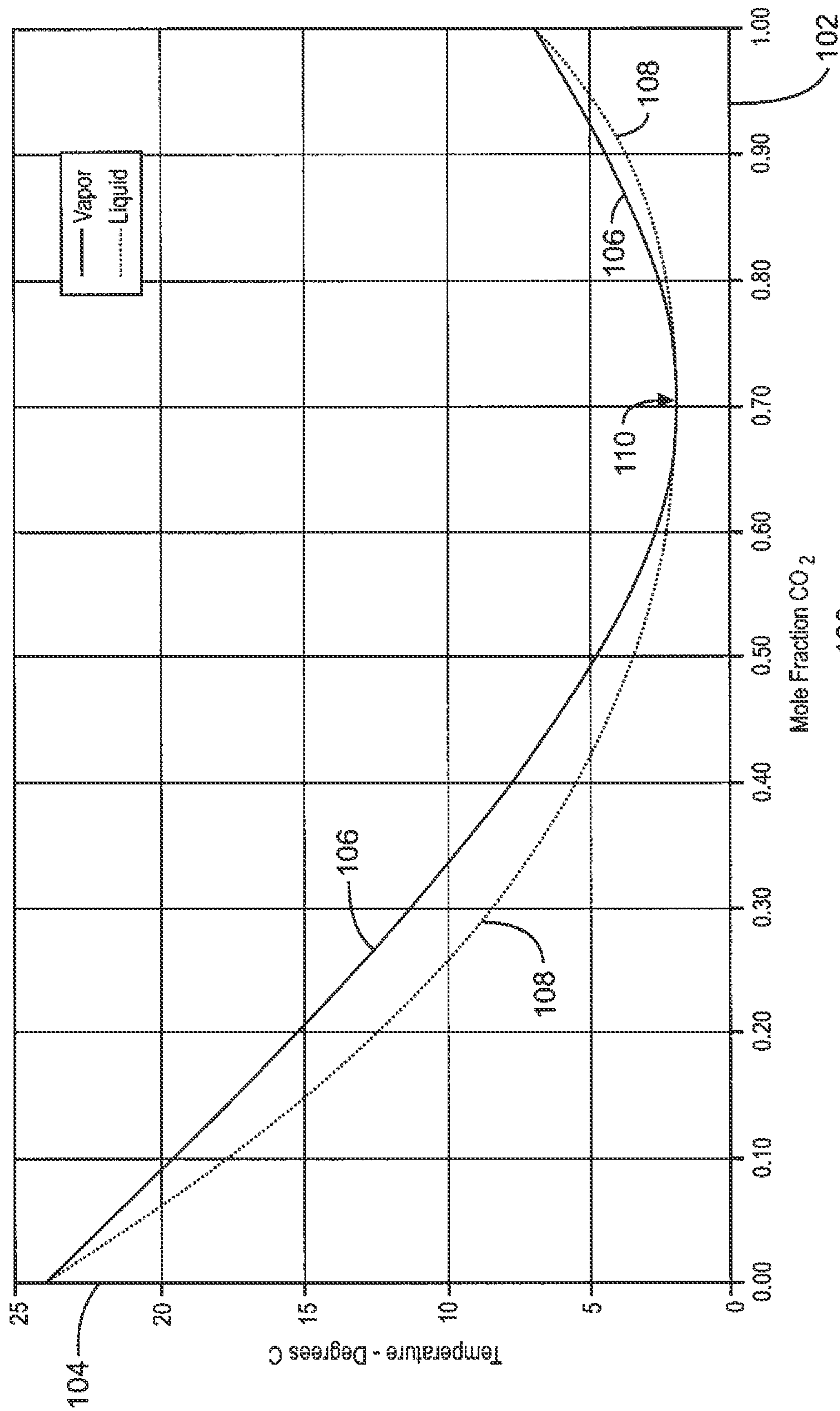
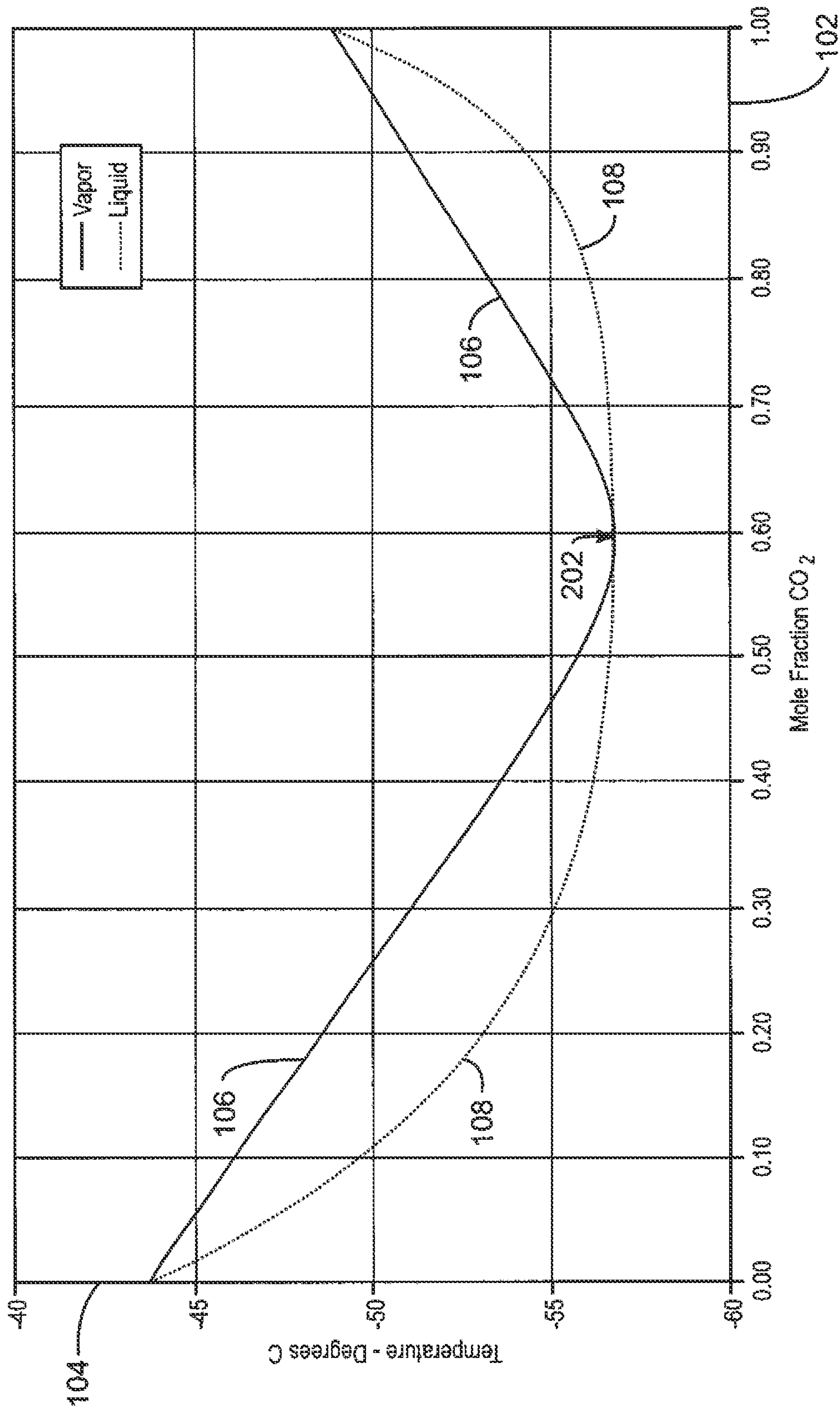
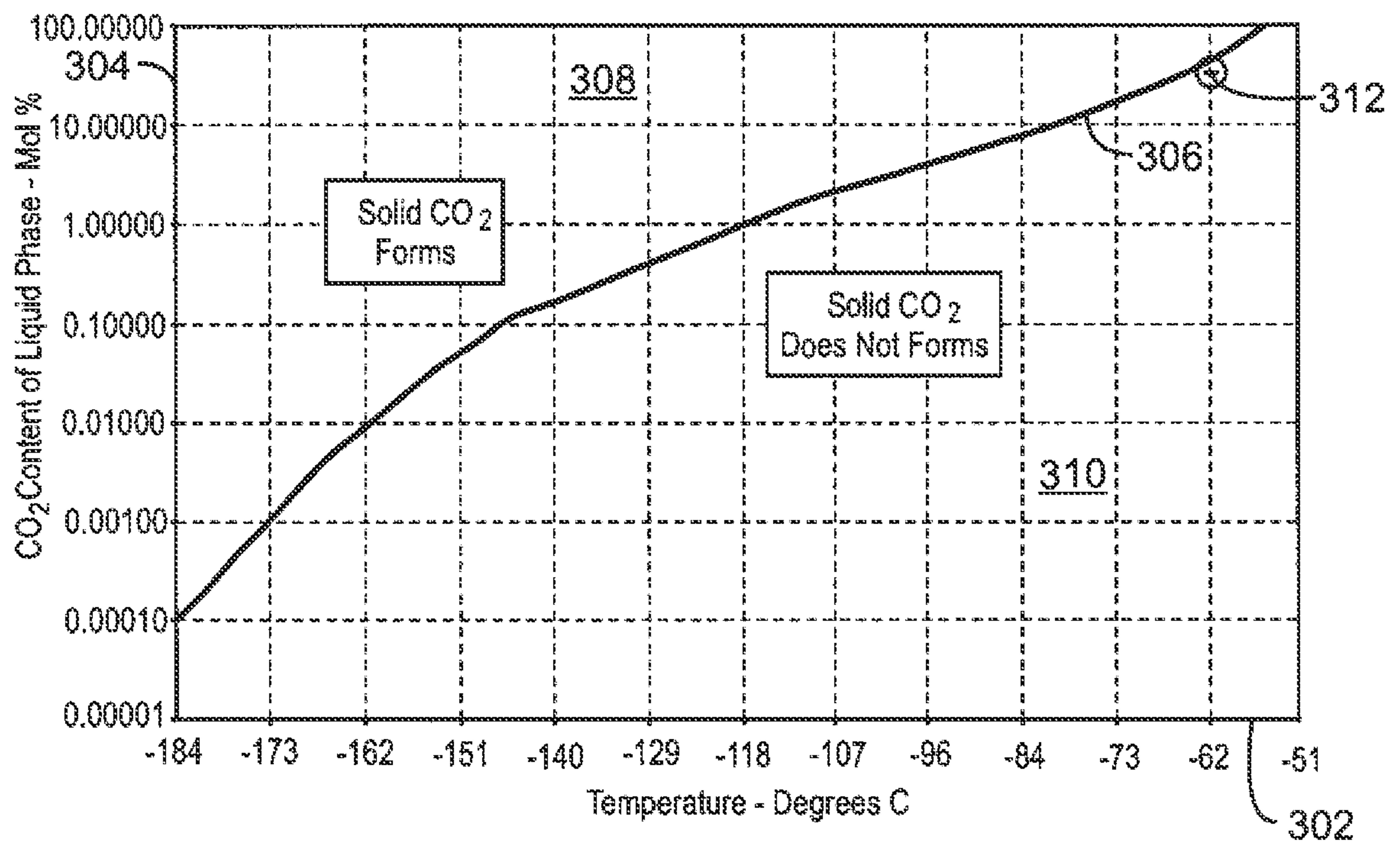


FIG. 1

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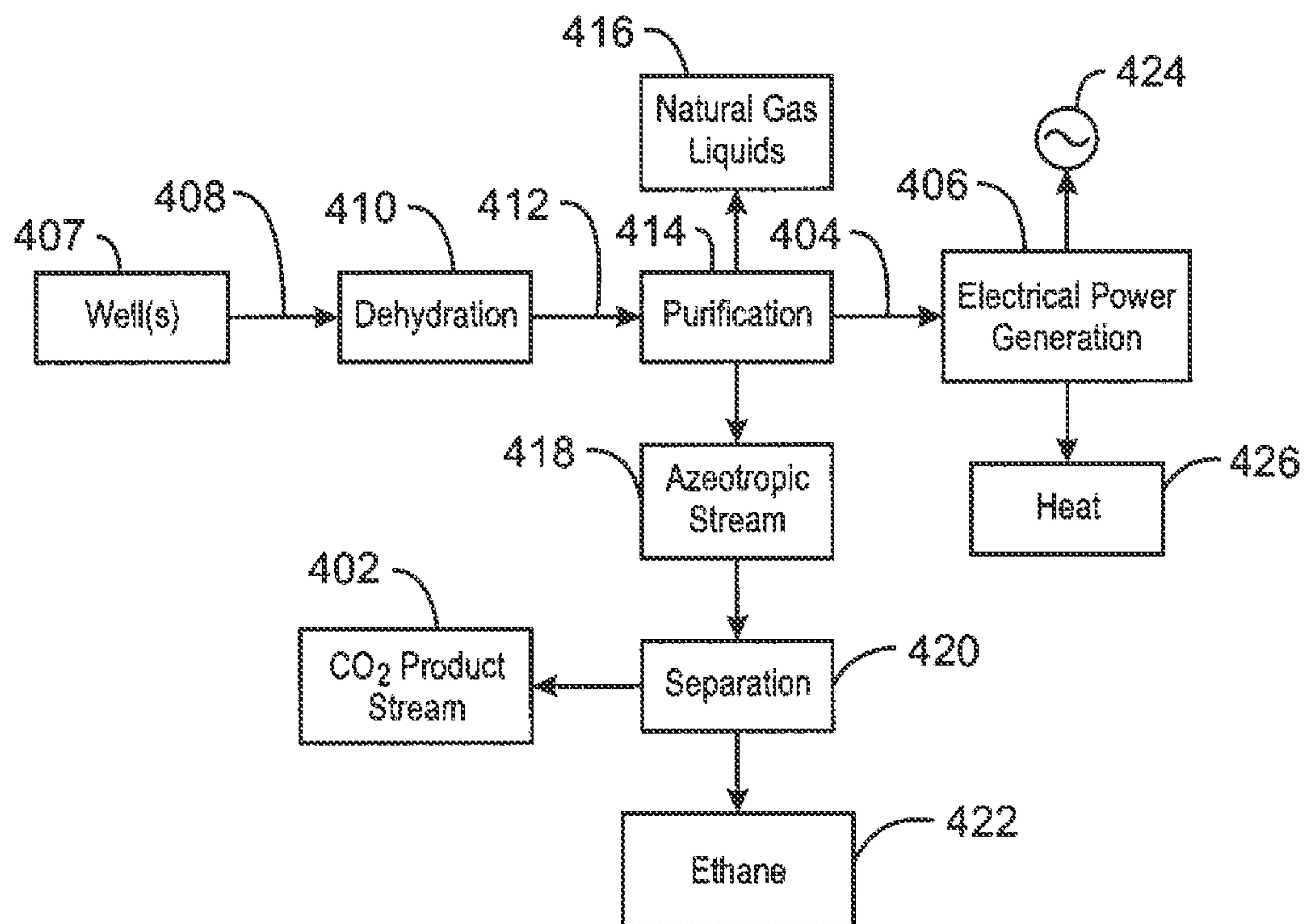


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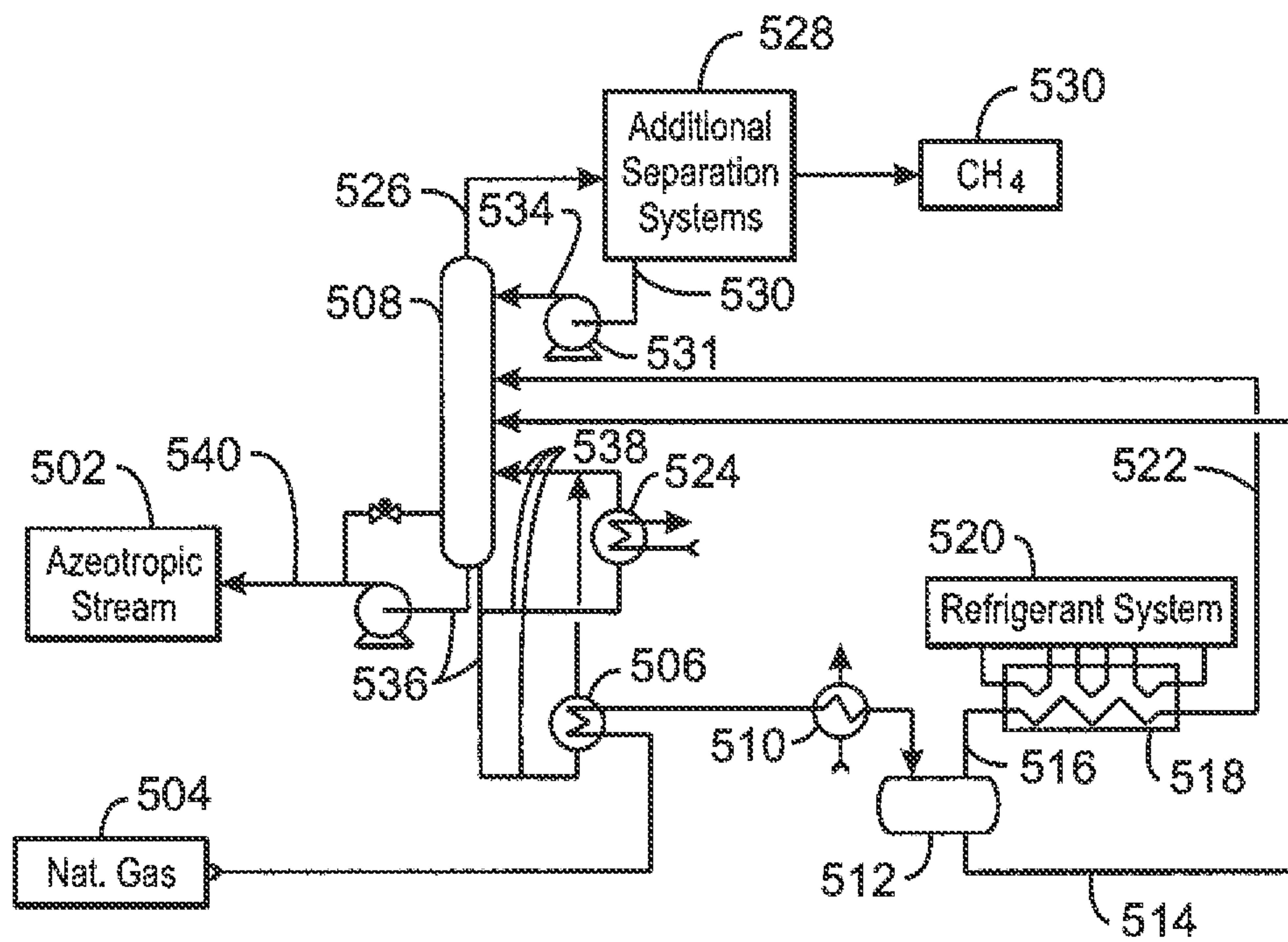
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FIG. 3

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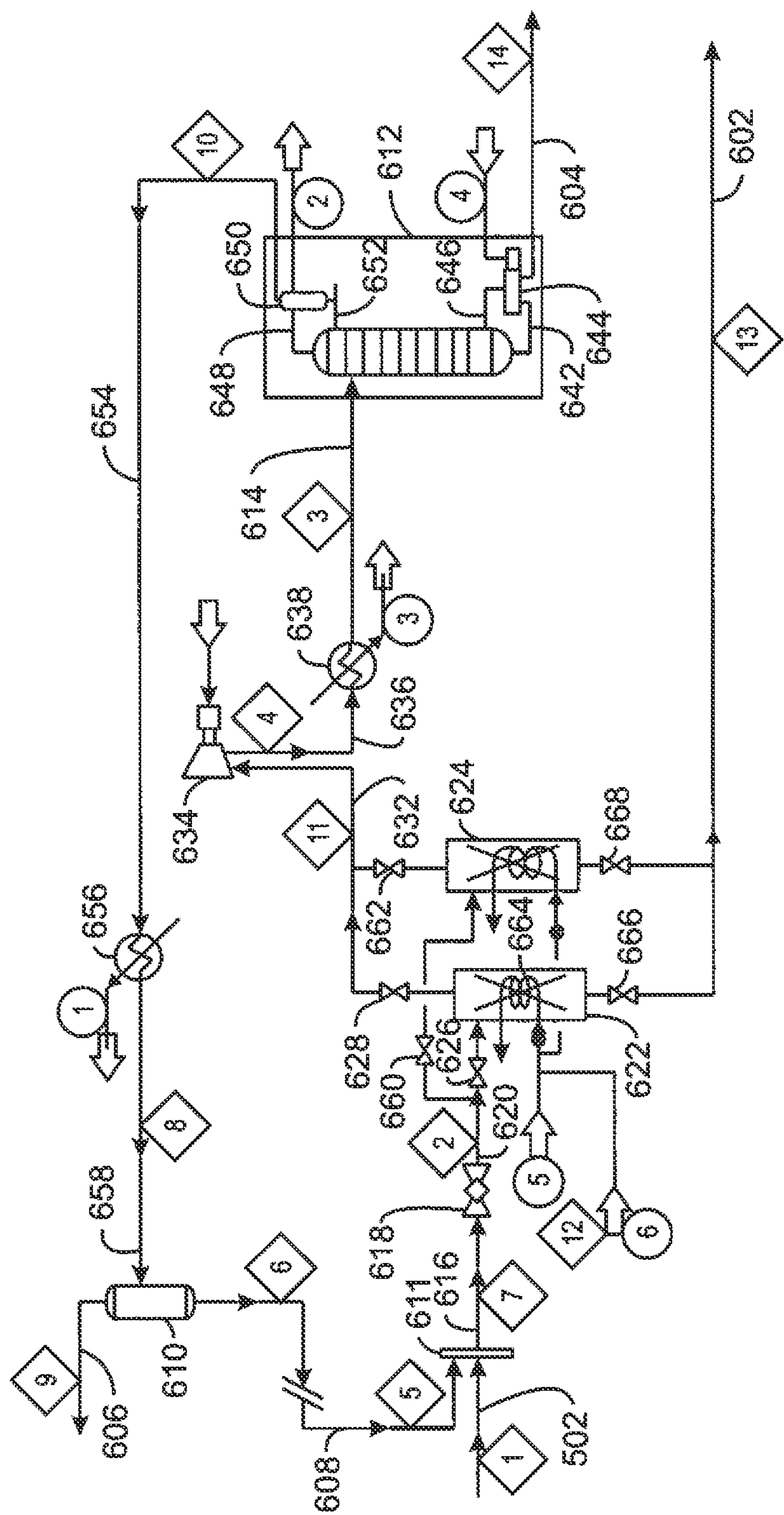
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FIG. 4

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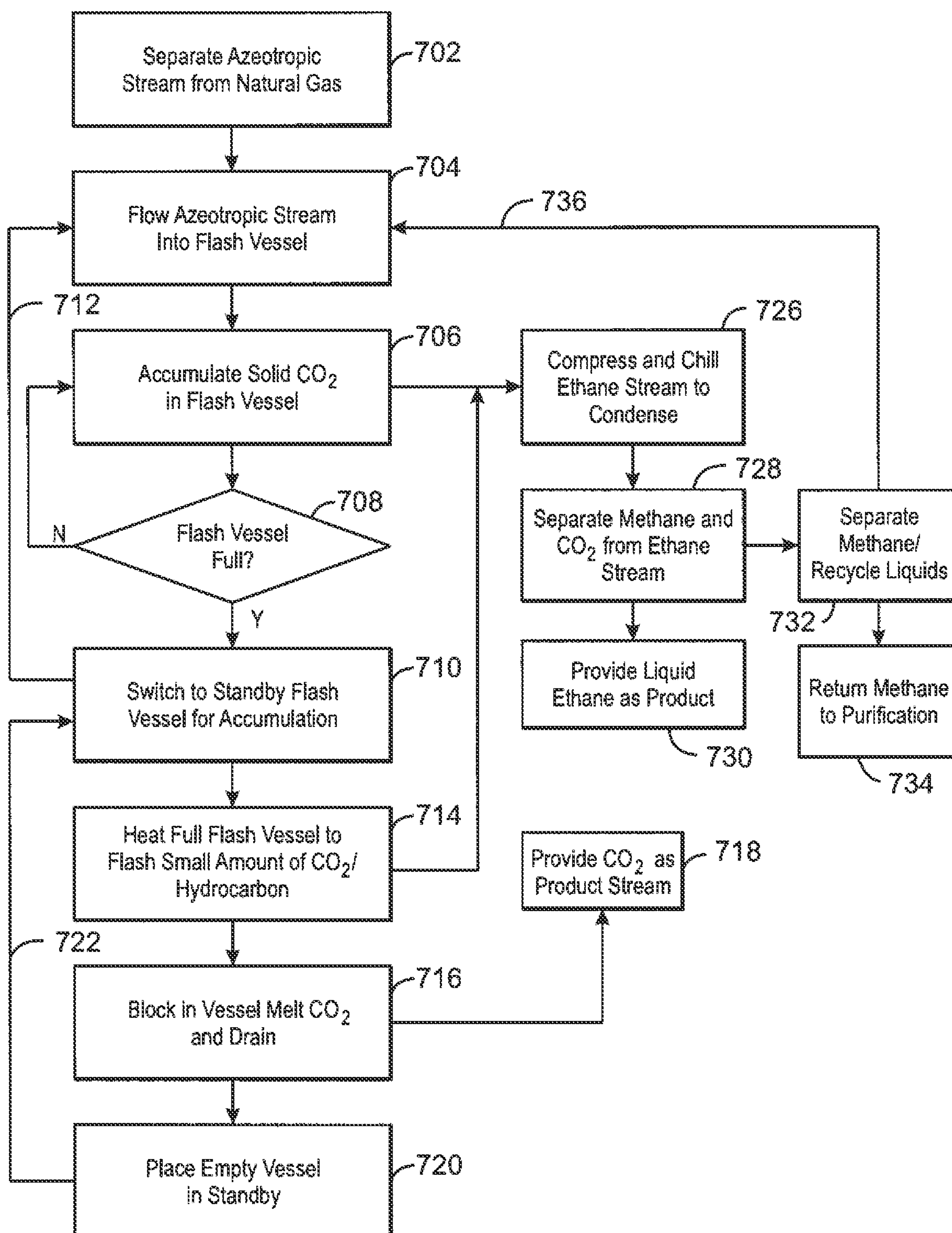
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FIG. 5

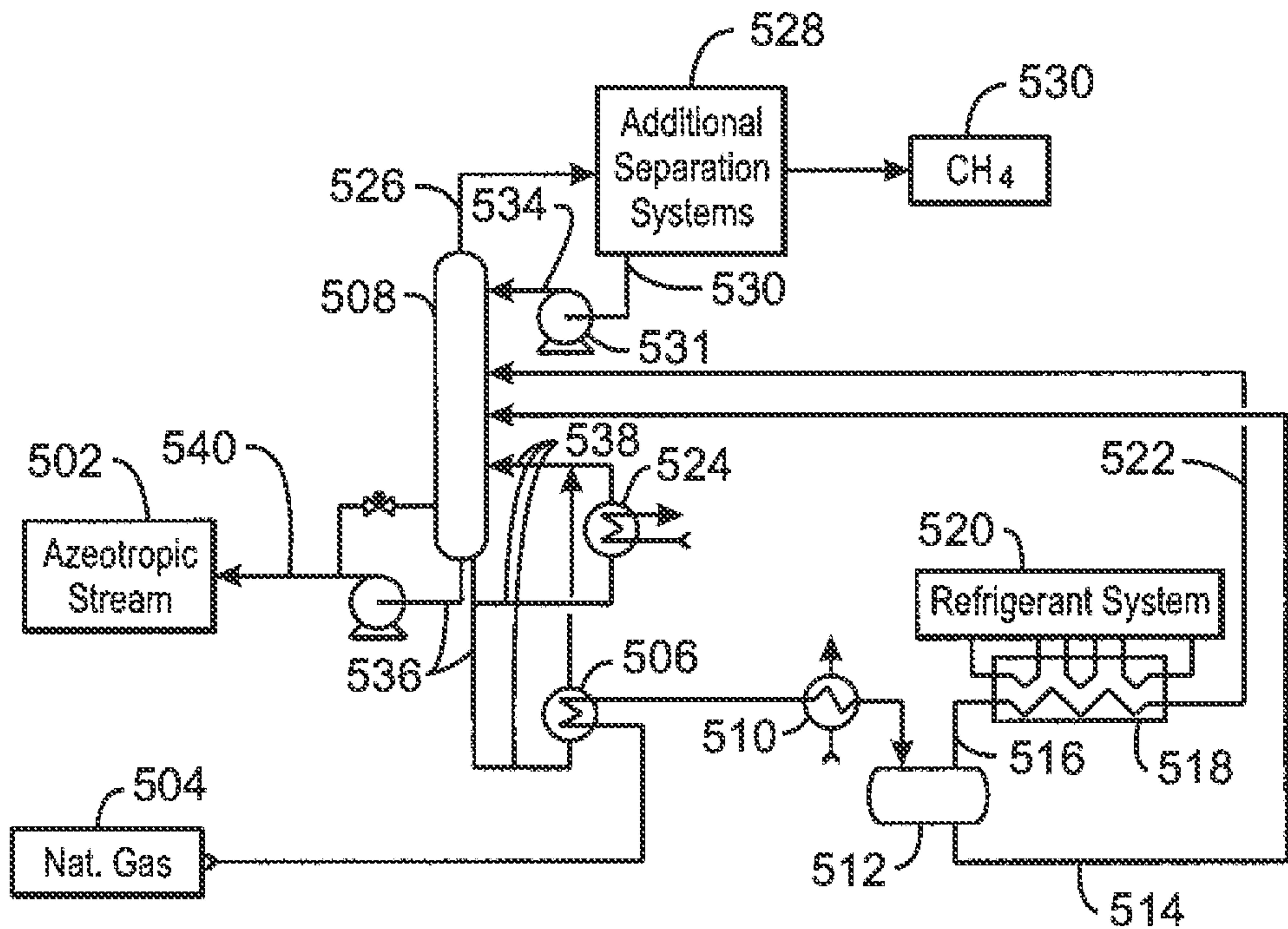
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600
FIG. 6

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700
FIG. 7



500
FIG. 5