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(54) **LIQUEFIED NATURAL GAS PRODUCTION**

(57) Hydrocarbon processing system and a method for liquefied natural gas (LNG) production are described herein. The hydrocarbon processing system includes a fluorocarbon refrigeration system configured to cool a natural gas to produce LNG using a mixed fluorocarbon

refrigerant, a nitrogen rejection unit (NRU) configured to remove nitrogen from the LNG; and an autorefrigeration system configured to further cool the natural gas to produce the LNG.

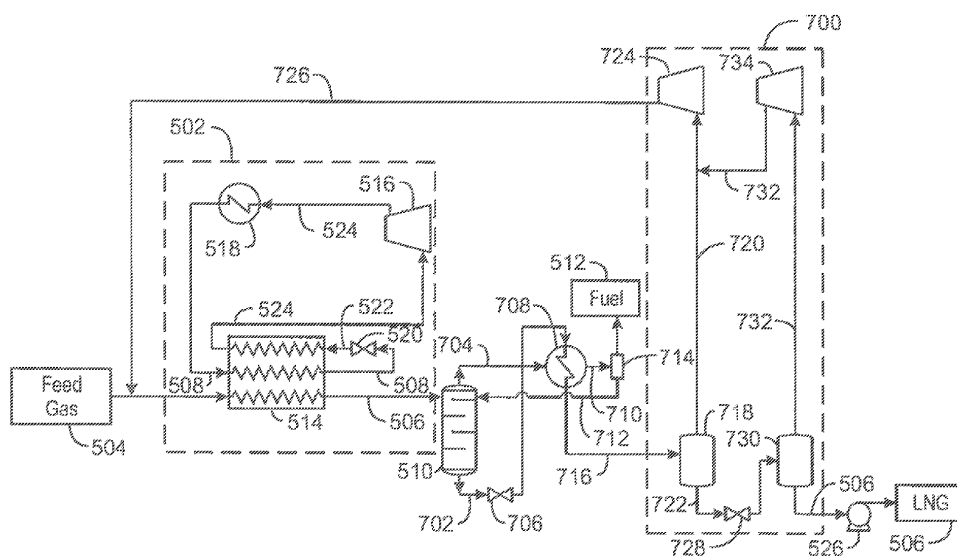


FIG. 7

Description**CROSS-REFERENCE TO RELATED APPLICATION**

5 **[0001]** This application claims the benefit of U.S. Provisional Patent Application 61/756,322 filed 24 January 2013 entitled LIQUEFIED NATURAL GAS PRODUCTION, the entirety of which is incorporated by reference herein.

FIELD OF THE INVENTION

10 **[0002]** The present techniques relate generally to the field of hydrocarbon recovery and treatment processes and, more particularly, to a method and systems for liquefied natural gas (LNG) production via a refrigeration process that uses mixed fluorocarbon refrigerants.

BACKGROUND

15 **[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.

20 **[0004]** Many low temperature refrigeration systems that are used for natural gas processing and liquefaction rely on the use of single component refrigerants or mixed refrigerants (MRs) including hydrocarbons components to provide external refrigeration. For example, liquefied natural gas (LNG) may be produced using a mixed refrigerant including hydrocarbon components extracted from a feed gas. Such hydrocarbon components may include methane, ethane, ethylene, propane, and the like.

25 **[0005]** U.S. Patent No. 6,412,302 to Foglietta et al. describes a process for producing a liquefied natural gas stream. The process includes cooling at least a portion of a pressurized natural gas feed stream by heat exchange contact with first and second expanded refrigerants that are used in independent refrigeration cycles. The first expanded refrigerant is selected from methane, ethane, and treated and pressurized natural gas, while the second expanded refrigerant is nitrogen. Therefore, such techniques rely on the use of refrigerants including hydrocarbons, which are flammable.

30 **[0006]** U.S. Patent Application Publication No. 2010/0281915 by Roberts et al. describes a system and method for liquefying a natural gas stream. A dehydrated natural gas stream is pre-cooled in a pre-cooling apparatus that uses a pre-coolant consisting of a HFC refrigerant. The pre-cooled dehydrated natural gas stream is then cooled in a main heat exchanger through indirect heat exchange against a vaporized hydrocarbon mixed refrigerant coolant to produce LNG. The mixed refrigerant coolant includes ethane, methane, nitrogen, and less than or equal to 3 mol % of propane. Therefore, such techniques also rely on the use of refrigerants including hydrocarbons.

35 **[0007]** U.S. Patent Application Publication No. 2012/0047943 by Barclay et al. describes a process for offshore liquefaction of a natural gas feed. The process includes contacting the natural gas feed with a biphasic refrigerant at a first temperature, contacting the natural gas feed with a first gaseous refrigerant at a second temperature, and contacting the natural gas feed with a second gaseous refrigerant at a third temperature. The refrigerated natural gas feed is then expanded using an expansion device to form a flash gas stream and a liquefied natural gas stream. The biphasic refrigerant may be a commercial refrigerant such as R507 or R134a, or a mixture thereof. The first gaseous refrigerant may be nitrogen. The second gaseous refrigerant may be the flash gas stream recovered from the natural gas feed. The biphasic refrigerant is used to cool and partially condense the natural gas feed in a feed gas chiller, while the first and second gaseous refrigerants are used to cool and condense the natural gas feed in a main cryogenic heat exchanger. Therefore, such techniques rely on the use of a refrigerant including hydrocarbon components extracted from the natural gas feed.

40 **[0008]** U.S. Patent No. 6,631,625 to Weng describes a non-hydrochlorofluorocarbon (non-HCFC) design of a refrigerant mixture for an ultra-low temperature refrigeration system. The non-HCFC refrigerant mixture is primarily composed of hydrofluorocarbon (HFC) refrigerants and hydrocarbons. Therefore, such techniques also rely on the use of refrigerants including hydrocarbons. Furthermore, the use of such refrigerant mixtures for natural gas processing or liquefaction is not disclosed.

SUMMARY

55 **[0009]** An embodiment provides a hydrocarbon processing system for liquefied natural gas (LNG) production. The hydrocarbon processing system includes a fluorocarbon refrigeration system configured to cool a natural gas to produce LNG using a mixed fluorocarbon refrigerant and a nitrogen rejection unit (NRU) configured to remove nitrogen from the LNG.

[0010] Another embodiment provides a method for liquefied natural gas (LNG) production. The method includes cooling a natural gas to produce LNG in a fluorocarbon refrigeration system using a mixed fluorocarbon refrigerant and removing nitrogen from the LNG in a nitrogen rejection unit (NRU).

[0011] Another embodiment provides a hydrocarbon processing system for the formation of a liquefied natural gas (LNG). The hydrocarbon processing system includes a mixed refrigerant cycle configured to cool a natural gas using a mixed fluorocarbon refrigerant, wherein the mixed refrigerant cycle includes a heat exchanger configured to allow for cooling of the natural gas via an indirect exchange of heat between the natural gas and the mixed fluorocarbon refrigerant. The hydrocarbon processing system also includes a nitrogen rejection unit (NRU) configured to remove nitrogen from the natural gas and a methane autorefrigeration system configured to cool the natural gas to produce the LNG.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:

Fig. 1 is a process flow diagram of a single stage refrigeration system;

Fig. 2 is a process flow diagram of a two stage refrigeration system including an economizer;

Fig. 3 is a process flow diagram of a single stage refrigeration system including a heat exchanger economizer;

Fig. 4 is a process flow diagram of a liquefied natural gas (LNG) production system;

Fig. 5 is a process flow diagram of a hydrocarbon processing system including a single mixed refrigerant (SMR) cycle;

Fig. 6 is a process flow diagram of the hydrocarbon processing system of Fig. 5 with the addition of a nitrogen refrigeration system;

Fig. 7 is a process flow diagram of the hydrocarbon processing system of Fig. 5 with the addition of a methane autorefrigeration system;

Fig. 8 is a process flow diagram of a hydrocarbon processing system including a pre-cooled SMR cycle;

Fig. 9 is a process flow diagram of a hydrocarbon processing system including a dual mixed refrigerant (DMR) cycle;

Figs. 10A and 10B are process flow diagrams of a hydrocarbon processing system including an SMR cycle, an NRU, and a methane autorefrigeration system;

Figs. 11A and 11B are process flow diagrams of a hydrocarbon processing system including an economized DMR cycle, an NRU, and a methane autorefrigeration system; and

Fig. 12 is a process flow diagram of a method for the formation of LNG from a natural gas stream using a mixed fluorocarbon refrigerant.

DETAILED DESCRIPTION

[0013] 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 for exemplary purposes only and simply provides a description of the exemplary embodiments. Accordingly, the techniques are not limited to the specific embodiments described herein, but rather, include all alternatives, modifications, and equivalents falling within the spirit and scope of the appended claims.

[0014] At the outset, for ease of reference, certain terms used in this application and their meanings as used in this context are set forth. To the extent a term used herein is not defined herein, 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 herein, as all equivalents, synonyms, new developments, and terms or techniques that serve the same or a similar purpose are considered to be within the scope of the present claims.

[0015] As used herein, "autorefrigeration" refers to a process whereby a portion of a product stream is used for

refrigeration purposes. This is achieved by extracting a fraction of the product stream prior to final cooling for the purpose of providing refrigeration capacity. This extracted stream is expanded in a valve or expander and, as a result of the expansion, the temperature of the stream is lowered. This stream is used for cooling the product stream in a heat exchanger. After exchanging heat, this stream is recompressed and blended with the feed gas stream. This process is also known as open cycle refrigeration.

[0016] Alternatively, "autorefrigeration" refers to a process whereby a fluid is cooled via a reduction in pressure. In the case of liquids, autorefrigeration refers to the cooling of the liquid by evaporation, which corresponds to a reduction in pressure. More specifically, a portion of the liquid is flashed into vapor as it undergoes a reduction in pressure while passing through a throttling device. As a result, both the vapor and the residual liquid are cooled to the saturation temperature of the liquid at the reduced pressure. For example, according to embodiments described herein, autorefrigeration of a natural gas may be performed by maintaining the natural gas at its boiling point so that the natural gas is cooled as heat is lost during boil off. This process may also be referred to as "flash evaporation."

[0017] The "boiling point" or "BP" of a substance is the temperature at which the vapor pressure of the liquid equals the pressure surrounding the liquid and, thus, the liquid changes into a vapor. The "normal boiling point" or "NBP" of a substance is the boiling point at a pressure of one atmosphere, i.e., 101.3 kilopascals (kPa).

[0018] A "compressor" includes any unit, device, or apparatus able to increase the pressure of a stream. This includes compressors having a single compression process or step, or compressors having multi-stage compression processes or steps, more particularly multi-stage compressors within a single casing or shell. Evaporated streams to be compressed can be provided to a compressor at different pressures. For example, some stages or steps of a hydrocarbon cooling process may involve two or more refrigerant compressors in parallel, series, or both. The present techniques are not limited by the type or arrangement or layout of the compressor or compressors, particularly in any refrigeration cycle.

[0019] As used herein, "cooling" broadly refers to lowering and/or dropping a temperature and/or internal energy of a substance, such as by any suitable amount. Cooling may include a temperature drop of at least about 1 °C, at least about 5 °C, at least about 10 °C, at least about 15 °C, at least about 25 °C, at least about 50 °C, at least about 100 °C, and/or the like. The cooling may use any suitable heat sink, such as steam generation, hot water heating, cooling water, air, refrigerant, other process streams (integration), and combinations thereof. One or more sources of cooling may be combined and/or cascaded to reach a desired outlet temperature. The cooling step may use a cooling unit with any suitable device and/or equipment. According to one embodiment, cooling may include indirect heat exchange, such as with one or more heat exchangers. Heat exchangers may include any suitable design, such as shell and tube, brazed aluminum, spiral wound, and/or the like. In the alternative, the cooling may use evaporative (heat of vaporization) cooling, sensible heat cooling, and/or direct heat exchange, such as a liquid sprayed directly into a process stream.

[0020] "Cryogenic temperature" refers to a temperature that is about -50 °C or below.

[0021] As used herein, the terms "deethanizer" and "demethanizer" refer to distillation columns or towers that may be used to separate components within a natural gas stream. For example, a demethanizer is used to separate methane and other volatile components from ethane and heavier components. The methane fraction is typically recovered as purified gas that contains small amounts of inert gases such as nitrogen, CO₂, or the like.

[0022] "Fluorocarbons," also referred to as "perfluorocarbons" or "PFCs," are molecules including F and C atoms. Fluorocarbons have F-C bonds and, depending on the number of carbon atoms in the species, C-C bonds. An example of a fluorocarbon includes hexafluoroethane (C₂F₆). "Hydrofluorocarbons" or "HFCs" are a specific type of fluorocarbon including H, F, and C atoms. Hydrofluorocarbons have H-C and F-C bonds and, depending on the number of carbon atoms in the species, C-C bonds. Some examples of hydrofluorocarbons include fluoroform (CHF₃), pentafluoroethane (C₂HF₅), tetrafluoroethane (C₂H₂F₄), heptafluoropropane (C₃HF₇), hexafluoropropane (C₃H₂F₆), pentafluoropropane (C₃H₃F₅), and tetrafluoropropane (C₃H₄F₄), among other compounds of similar chemical structure. Hydrofluorocarbons with unsaturated bonds are referred to as "hydrofluoroolefins" or "HFOs." HFOs are typically more reactive and flammable than HFCs due to the presence of unsaturated bonds. However, HFOs also typically degrade in the environment faster than HFCs.

[0023] The term "gas" is used interchangeably with "vapor," and is defined as 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.

[0024] The term "greenhouse gases" broadly refers to gases or vapors in an atmosphere that can absorb and/or emit radiation within the thermal infrared range. Examples include carbon monoxide, carbon dioxide, water vapor, methane, ethane, propane, ozone, hydrogen sulfide, sulfur oxides, nitrogen oxides, halocarbons, chlorofluorocarbons, or the like. Electrical power plants, petroleum refineries, and other energy conversion facilities can tend to be large sources of greenhouse gases emitted to the atmosphere. Without being bound by theory, greenhouse gases are believed to receive and/or retain solar radiation and energy, which become trapped in the atmosphere. This may result in an increase in average global atmospheric temperatures and other climate changes.

[0025] The "global-warming potential" or "GWP" of a gas is a relative measure of how much heat the gas traps in the atmosphere. GWP compares the amount of heat trapped by a certain mass of the gas in question to the amount of heat

trapped by a similar mass of carbon dioxide. GWP is calculated over a specific time interval, such as 20, 100 or 500 years. GWP is expressed as a factor of carbon dioxide, wherein carbon dioxide has a standardized GWP of 1. For example, the 20 year GWP, *i.e.*, GWP₂₀, of methane is 72. This means that, if the same mass of methane and carbon dioxide are introduced into the atmosphere, the methane will trap 72 times more heat than the carbon dioxide over the next 20 years.

[0026] A "heat exchanger" broadly means any device capable of transferring heat from one media to another media, including particularly any structure, *e.g.*, device commonly referred to as a heat exchanger. Heat exchangers include "direct heat exchangers" and "indirect heat exchangers." Thus, a heat exchanger may be a shell-and-tube, spiral, hairpin, core, core-and-kettle, double-pipe, brazed aluminum, spiral wound, or any other type of known heat exchanger. "Heat exchanger" may also refer to any column, tower, unit or other arrangement adapted to allow the passage of one or more streams there through, and to affect direct or indirect heat exchange between one or more lines of refrigerant, and one or more feed streams.

[0027] A "hydrocarbon" is an organic compound that primarily includes the elements 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 components found in natural gas, oil, or chemical processing facilities.

[0028] "Liquefied natural gas" or "LNG" is natural gas generally known to include a high percentage of methane. However, LNG may also include trace amounts of other compounds. The other elements or compounds may include, but are not limited to, ethane, propane, butane, carbon dioxide, nitrogen, helium, hydrogen sulfide, or combinations thereof, that have been processed to remove one or more components (for instance, helium) or impurities (for instance, water and/or heavy hydrocarbons) and then condensed into a liquid at almost atmospheric pressure by cooling.

[0029] "Liquefied petroleum gas" or "LPG" generally refers to a mixture of propane, butane, and other light hydrocarbons derived from refining crude oil. At normal temperature, LPG is a gas. However, LPG can be cooled or subjected to pressure to facilitate storage and transportation.

[0030] The "melting point" or "MP" of a substance is the temperature at which the solid and liquid forms of the substance can exist in equilibrium. As heat is applied to the solid form of a substance, its temperature will increase until the melting point is reached. The application of additional heat will then convert the substance from solid form to liquid form with no temperature change. When the entire substance has melted, additional heat will raise the temperature of the liquid form of the substance.

[0031] "Mixed refrigerant processes" or "MR processes" may include, but are not limited to, a "single mixed refrigerant" or "SMR" cycle, a hydrocarbon pre-cooled MR cycle, a "dual mixed refrigerant" or "DMR" cycle, and a "triple mixed refrigerant" or "TMR" cycle. In general, MRs can include hydrocarbon and/or non-hydrocarbon components. MR processes employ at least one mixed component refrigerant, but can additionally employ one or more pure-component refrigerants as well.

[0032] "Natural gas" refers to a multi-component gas obtained from a crude oil well or from a subterranean gas-bearing formation. The composition and pressure of natural gas can vary significantly. A typical natural gas stream contains methane (CH₄) as a major component, *i.e.*, greater than 50 mol % of the natural gas stream is methane. The natural gas stream can also contain ethane (C₂H₆), higher molecular weight hydrocarbons (*e.g.*, C₃-C₂₀ hydrocarbons), one or more acid gases (*e.g.*, carbon dioxide or hydrogen sulfide), or any combinations thereof. The natural gas can also contain minor amounts of contaminants such as water, nitrogen, iron sulfide, wax, crude oil, or any combinations thereof. The natural gas stream may be substantially purified prior to use in embodiments, so as to remove compounds that may act as poisons.

[0033] As used herein, "natural gas liquids" or "NGLs" refer to mixtures of hydrocarbons whose components are, for example, typically heavier than methane and condensed from a natural gas. Some examples of hydrocarbon components of NGL streams include ethane, propane, butane, and pentane isomers, benzene, toluene, and other aromatic compounds.

[0034] A "nitrogen rejection unit" or "NRU" refers to any system or device configured to receive a natural gas feed stream and produce substantially pure products streams, *e.g.*, a salable methane stream and a nitrogen stream including about 30% to 99% N₂. Examples of types of NRU's include cryogenic distillation, pressure swing adsorption (PSA), membrane separation, lean oil absorption, and solvent absorption.

[0035] The "ozone depletion potential" or "ODP" of a chemical compound is the relative amount of degradation to the ozone layer it can cause, where trichlorofluoromethane, *i.e.*, R-1, is fixed at an ODP of 1.0. Chlorodifluoromethane, *i.e.*, R-22, for example, has an ODP of 0.055. Many HFCs, such as R-32, have ODPs approaching zero.

[0036] A "refrigerant component," in a refrigeration system, will absorb heat at a lower temperature and pressure through evaporation and will reject heat at a higher temperature and pressure through condensation. Illustrative refrigerant components may include, but are not limited to, alkanes, alkenes, and alkynes having one to five carbon atoms, nitrogen, chlorinated hydrocarbons, fluorinated hydrocarbons, other halogenated hydrocarbons, noble gases, and mixtures or combinations thereof.

[0037] Refrigerant components often include single component refrigerants. A single component refrigerant with a

single halogenated hydrocarbon has an associated "R-" designation of two or three numbers, which reflects its chemical composition. Adding 90 to the number gives three digits that stand for the number of carbon, hydrogen, and fluorine atoms, respectively. The first digit of a refrigerant with three numbers is one unit lower than the number of carbon atoms in the molecule. If the molecule contains only one carbon atom, the first digit is omitted. The second digit is one unit greater than the number of hydrogen atoms in the molecule. The third digit is equal to the number of fluorine atoms in the molecule. Remaining bonds not accounted for are occupied by chlorine atoms. A suffix of a lower-case letter "a," "b," or "c" indicates increasingly unsymmetrical isomers. As a special case, the R-400 series is made up of zeotropic blends, and the R-500 series is made up of azeotropic blends. The rightmost digit is assigned arbitrarily by ASHRAE, an industry organization.

[0038] "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 depend, in some cases, on the specific context.

Overview

[0039] Embodiments described herein provide a hydrocarbon processing system. The hydrocarbon processing system includes a refrigeration system for producing LNG from a natural gas. The refrigeration system includes a fluorocarbon refrigeration system that utilizes a mixed fluorocarbon refrigerant to cool the natural gas. The refrigeration system may also include a nitrogen refrigeration system and/or a methane autorefrigeration system, which may be used to further cool the natural gas to produce LNG. In addition, the hydrocarbon processing system may include an NRU, which may be used to remove nitrogen from the natural gas. In some embodiments, the nitrogen that is removed from the natural gas via the NRU is used to provide additional cooling for the natural gas.

[0040] Hydrocarbon processing systems include any number of systems known to those skilled in the art. Hydrocarbon production and treatment processes include, but are not limited to, chilling natural gas for NGL extraction, chilling natural gas for hydrocarbon dew point control, chilling natural gas for CO₂ removal, LPG production storage, condensation of reflux in deethanizers or demethanizers, and natural gas liquefaction to produce LNG.

[0041] Although many refrigeration cycles have been used to process hydrocarbons, one cycle that is used in LNG liquefaction plants is the cascade cycle, which uses multiple single component refrigerants in heat exchangers arranged progressively to reduce the temperature of the gas to a liquefaction temperature. Another cycle that is used in LNG liquefaction plants is the multi-component refrigeration cycle, which uses a multi-component refrigerant in specially designed exchangers. In addition, another cycle that is used in LNG liquefaction plants is the expander cycle, which expands gas from feed gas pressure to a low pressure with a corresponding reduction in temperature. Natural gas liquefaction cycles may also use variations or combinations of these three cycles.

[0042] LNG is prepared from a feed gas by refrigeration and liquefaction technologies. Optional steps include condensate removal, CO₂ removal, dehydration, mercury removal, nitrogen stripping, H₂S removal, and the like. After liquefaction, LNG may be stored or loaded on a tanker for sale or transport. Conventional liquefaction processes can include: APCI Propane pre-cooled mixed refrigerant; C3MR; DUAL MR; Phillips Optimized Cascade; Prico SMR; TEAL dual pressure mixed refrigerant; Linde/Statoil multi fluid cascade; Axens DMR; ExxonMobil's Enhanced Mixed Refrigerant (EMR); and the Shell processes C3MR and DMR.

[0043] Carbon dioxide removal, i.e., separation of methane and lighter gases from CO₂ and heavier gases, may be achieved with cryogenic distillation processes, such as the Controlled Freeze Zone technology available from ExxonMobil Corporation.

[0044] While the method and systems described herein are discussed with respect to the formation of LNG from natural gas, the method and systems may also be used for a variety of other purposes. For example, the method and systems described herein may be used to chill natural gas for hydrocarbon dew point control, perform natural gas liquid (NGL) extraction, separate methane and lighter gases from CO₂ and heavier gases, prepare hydrocarbons for LPG production, or condense a reflux stream in deethanizers and/or demethanizers, among others.

Refrigerants

[0045] The refrigerants that are utilized according to embodiments described herein may be mixed refrigerants, where each mixed refrigerant may include two or more single component and/or multicomponent refrigerants. Refrigerants may be imported and stored on-site or, alternatively, some of the components of the refrigerant may be prepared on-site, typically by a distillation process integrated with the hydrocarbon processing system. In various embodiments, the mixed refrigerants that are utilized according to embodiments described herein include fluorocarbons (FCs), such as HFCs. Exemplary refrigerants are commercially available from DuPont Corporation, including the ISCEON® family of refrigerants, the SUVA® family of refrigerants, the OPTEON® family of refrigerants, and the FREON® family of refrigerants.

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[0046] Multicomponent refrigerants are commercially available. For example, R-401A is a HCFC blend of R-32, R-152a, and R-124. R-404A is a HFC blend of 52 wt.% R-143a, 44 wt.% R-125, and 4 wt.% R-134a. R-406A is a blend of 55 wt.% R-22, 4 wt.% R-600a, and 41 wt.% R-142b. R-407A is a HFC blend of 20 wt.% R-32, 40 wt.% R-125, and 40 wt.% R-134a. R-407C is a hydrofluorocarbon blend of R-32, R-125, and R-134a. R-408A is a HCFC blend of R-22, R-125, and R-143a. R-409A is a HCFC blend of R-22, R-124, and R-142b. R-410A is a blend of R-32 and R-125. R-500 is a blend of 73.8 wt.% R-12 and 26.2 wt.% of R-152a. R-502 is a blend of R-22 and R-115. R-508B is a blend of R-23 and R-116. More specific information regarding particular refrigerants that may be used according to embodiments described herein is shown below in Table 1.

[0047] The ozone depletion potentials for all the refrigerants shown in Table 1 are equal to zero. The "Safety Group" shown in Table 1 is an ASHRAE designation. A designation of "A" indicates that the Occupational Exposure Limit (OEL) for the refrigerant is above 400 parts per million (ppm). A designation of "B" indicates that the OEL for the refrigerant is below 400 ppm. A number of "1" indicates that the refrigerant is non-flammable. A number of "2" indicates that the refrigerant is slightly flammable, and a number of "3" indicates that the refrigerant is highly flammable. An "L" suffix indicates that the refrigerant has a very low flame propagation speed.

[0048] It is to be understood that the embodiments described herein are not limited to the use of the refrigerants listed in Table 1. Rather, any other suitable types of non-flammable refrigerants, or mixtures thereof, may also be used according to embodiments described herein. For example, any suitable types of HFCs, HFOs, and/or inert compounds can be combined to form a mixed refrigerant according to embodiments described herein.

TABLE 1: Refrigerants

ASHRAE Number	Chemical Name	Formula	MW	NBP °C	MP °C	Safety Group	Atm. Life years	GWP ₁₀₀
R-50	Methane	CH ₄	16	-162	-182	A3	12	25
R-14	Tetrafluoro methane	CF ₄	88	-128	-183	A1	50,000	7,390
R-23	Trifluoro methane	CHF ₃	70	-82	-155	A1	270	14,800
R-41	Fluoro methane	CH ₃ F	34	-78	-142	A3	2.4	92
R-32	Difluoro methane	CH ₂ F ₂	52	-52	-136	A2L	4.9	675
R-218	Octafluoro propane	C ₃ F ₈	188	-37	-148	A1	2,600	8,830
R-227ea	1,1,1,2,3,3,3-heptafluoro propane	CF ₃ CFHCF ₃	170	-16	-131	A1	34.2	3,220
R-245fa	1,1,1,3,3-pentafluoro propane	CF ₃ CH ₂ CHF ₂	134	15	-102	B1	7.6	1,030
R-116	Hexafluoro ethane	C ₂ F ₆	138	-78	-101	A1	10,000	12,200
R-125	1,1,1,2,2-Pentafluoro ethane	C ₂ HF ₅	120	-49	-103	A1	29	3,500
R-143a	1,1,1-trifluoro ethane	CH ₃ CF ₃	84	-48	-111	A2L	52	4,470
R-1234yf	2,3,3,3-Tetrafluoropropene	C ₃ H ₂ F ₄	114	-29	-152	A2L	0.03	0
R-134a	1,1,1,2-tetrafluoro ethane	CH ₂ FCF ₃	102	-26	-103	A1	14	1,430
R-152a	1,1difluoro ethane	CH ₂ CHF ₂	66	-25	-117	A2	1.4	124
R-1234ze	1,3,3,3-Tetrafluoropropene	C ₃ H ₂ F ₄	114	-19	-	A2L	-	0
R-C318	Octafluoro cyclobutane	(-CF ₂ -) ₄	200	-6	-40	A1	3,200	10,300
R-236fa	1,1,1,3,3,3-hexafluoro propane	CF ₃ CH ₂ CF ₃	152	-2	-96	A1	240	9,810

(continued)

ASHRAE Number	Chemical Name	Formula	MW	NBP °C	MP °C	Safety Group	Atm. Life years	GWP ₁₀₀
R-245ca	1,1,2,2,3-pentafluoro propane	CHF ₂ CF ₂ CH ₂ F	134	25	-82	B1	6.2	693
HFE-347mcc	Heptafluoropropyl, methyl ether	C ₃ F ₇ OCH ₃	200	34	-123	-	4.9	0
R-728	Nitrogen (non-HFC)	N ₂	28	-196	-210	A1	∞	0
R-740	Argon (non-HFC)	Ar	40	-186	-189	A1	∞	0
R-784	Krypton (non-HFC)	Kr						
-	Xenon (non-HFC)	Xe						
R-744	Carbon dioxide (non-HFC)	CO ₂	44	-57	-78	A1	33,000	1

[0049] According to embodiments described herein, the particular selection of fluorocarbons for a mixed refrigerant depends on the desired refrigeration temperatures. Natural gas liquefies to form LNG at -162 °C. Therefore, in order to produce LNG, a mixed refrigerant that is capable of chilling natural gas below -162 °C may be selected. In some cases, refrigerants may be used at warmer temperatures, and another refrigeration process, such as an autorefrigeration process, may be used to aid in the production of LNG.

[0050] When selecting a set of fluorocarbons for a mixed refrigerant, the normal boiling point and the melting point may both be taken into consideration. It may be desirable for the temperature of the mixed refrigerant to be above its freezing point during the entire refrigeration cycle, so that the refrigerant will not form solids and cause plugging in the system. In addition, it may be desirable to be above atmospheric pressure during the entire refrigeration cycle to avoid air contamination of the mixed refrigerant. In various embodiments, the components of the mixed refrigerant are selected such that the melting point of each component is below the chilling temperature. There may be some degree of flexibility in the melting point of the components, since a mixture does not start to freeze at the warmest pure component melting point. Some melting point depression occurs when a high melting point component is diluted in other, non-freezing components and approaches the eutectic point. For example, R-245fa, which has a melting point of -102 °C, can be used at lower temperatures if it is at a sufficiently low concentration in the mixed refrigerant.

[0051] The particular selection of fluorocarbons for a mixed refrigerant may also depend on the specific type of refrigeration system for which the mixed refrigerant is to be used. For example, SMR cycles may use mixed refrigerants including a mixture of R-14, R-23, R-32, R-227ea, R-245fa, or the like. Other possible refrigerant components for the mixed refrigerant include R-41, R-218, R-1234yf, R-1234ze, R-152a, and the like. In general, the components of a mixed refrigerant may be selected such that their NBPs evenly cover the desired refrigeration range.

[0052] In various embodiments, any of a number of different types of hydrocarbon processing systems can be used with any of the refrigeration systems described herein. In addition, the refrigeration systems described herein may utilize any mixture of the refrigerants described herein.

Refrigeration Systems

[0053] Hydrocarbon systems and methods often include refrigeration systems that utilize mechanical refrigeration, valve expansion, turbine expansion, or the like. Mechanical refrigeration typically includes compression systems and absorption systems, such as ammonia absorption systems. Compression systems are used in the gas processing industry for a variety of processes. For example, compression systems may be used for chilling natural gas for NGL extraction, chilling natural gas for hydrocarbon dew point control, LPG production storage, condensation of reflux in deethanizers or demethanizers, natural gas liquefaction to produce LNG, or the like.

[0054] Fig. 1 is a process flow diagram of a single stage refrigeration system 100. In various embodiments, the single stage refrigeration system 100 uses a mixed fluorocarbon refrigerant. The use of a mixed fluorocarbon refrigerant may allow the single stage refrigeration system 100 to maintain high efficiency over a wide range of temperatures. Further, in various embodiments, the single stage refrigeration system 100 is implemented upstream of a nitrogen refrigeration system or methane autorefrigeration system including an NRU. Multiple single stage refrigeration systems 100 may also be implemented in series upstream of such a nitrogen refrigeration system or methane autorefrigeration system.

[0055] The single stage refrigeration system 100 includes an expansion device 102, a chiller 104, a compressor 106,

a condenser 108, and an accumulator 110. The expansion device 102 may be an expansion valve or a hydraulic expander, for example. A saturated liquid refrigerant 112 may flow from the accumulator 110 to the expansion device 102, and may expand across the expansion device 102 isenthalpically. On expansion, some vaporization occurs, creating a chilled refrigerant mixture 114 that includes both vapor and liquid. The refrigerant mixture 114 may enter the chiller 104, also known as the evaporator, at a temperature lower than the temperature to which a process stream 116, such as a natural gas, is to be cooled. The process stream 116 flows through the chiller 104 and exchanges heat with the refrigerant mixture 114. As the process stream 116 exchanges heat with the refrigerant mixture 114, the process stream 116 is cooled, while the refrigerant mixture 114 vaporizes, creating a saturated vapor refrigerant 118.

[0056] After leaving the chiller 104, the saturated vapor refrigerant 118 is compressed within the compressor 106, and is then flowed into the condenser 108. Within the condenser 108, the saturated vapor refrigerant 118 is converted to a saturated, or slightly sub-cooled, liquid refrigerant 120. The liquid refrigerant 120 may then be flowed from the condenser 108 to the accumulator 110. The accumulator 110, which is also known as a surge tank or receiver, may serve as a reservoir for the liquid refrigerant 120. The liquid refrigerant 120 may be stored within the accumulator 110 before being expanded across the expansion device 102 as the saturated liquid refrigerant 112.

[0057] It is to be understood that the process flow diagram of Fig. 1 is not intended to indicate that the single stage refrigeration system 100 is to include all the components shown in Fig. 1. Further, the single stage refrigeration system 100 may include any number of additional components not shown in Fig. 1, depending on the details of the specific implementation. For example, in some embodiments, a refrigeration system can include two or more compression stages. In addition, the refrigeration system 100 may include an economizer, as discussed further with respect to Fig. 2.

[0058] Fig. 2 is a process flow diagram of a two stage refrigeration system 200 including an economizer 202. Like numbered items are as described with respect to Fig. 1. In various embodiments, the two stage refrigeration system 200 utilizes a fluorocarbon refrigerant, such as an azeotrope (R-5XX) or a near-azeotrope (R-4XX). Further, in various embodiments, the two stage refrigeration system 200 is implemented upstream of a nitrogen refrigeration system or methane autorefrigeration system including an NRU. Multiple two stage refrigeration systems 200 may also be implemented in series upstream of such a nitrogen refrigeration system or methane autorefrigeration system.

[0059] The economizer 202 may be any device or process modification that decreases the compressor power usage for a given chiller duty. Conventional economizers 202 include, for example, flash tanks and heat exchange economizers. Heat exchange economizers utilize a number of heat exchangers to transfer heat between process streams. This may reduce the amount of energy input into the two stage refrigeration system 200 by heat integrating process streams with each other.

[0060] As shown in Fig. 2, the saturated liquid refrigerant 112 leaving the accumulator 110 may be expanded across the expansion device 102 to an intermediate pressure at which vapor and liquid may be separated. For example, as the saturated liquid refrigerant 112 flashes across the expansion device 102, a vapor refrigerant 204 and a liquid refrigerant 206 are produced at a lower pressure and temperature than the saturated liquid refrigerant 112. The vapor refrigerant 204 and the liquid refrigerant 206 may then be flowed into the economizer 202. In various embodiments, the economizer 202 is a flash tank that effects the separation of the vapor refrigerant 204 and the liquid refrigerant 206. The vapor refrigerant 204 may be flowed to an intermediate pressure compressor stage, at which the vapor refrigerant 204 may be combined with saturated vapor refrigerant 118 exiting a first compressor 210, creating a mixed saturated vapor refrigerant 208. The mixed saturated vapor refrigerant 208 may then be flowed into a second compressor 212.

[0061] From the economizer 202, the liquid refrigerant 206 may be isenthalpically expanded across a second expansion device 214. The second expansion device 214 may be an expansion valve or a hydraulic expander, for example. On expansion, some vaporization may occur, creating a refrigerant mixture 216 that includes both vapor and liquid, lowering the temperature and pressure. The refrigerant mixture 216 will have a higher liquid content than refrigerant mixtures in systems without economizers. The higher liquid content may reduce the refrigerant circulation rate and/or reduce the power usage of the first compressor 210.

[0062] The refrigerant mixture 216 enters the chiller 104, also known as the evaporator, at a temperature lower than the temperature to which the process stream 116 is to be cooled. The process stream 116 is cooled within the chiller 104, as discussed with respect to Fig. 1. In addition, the saturated vapor refrigerant 118 is flowed through the compressors 210 and 212 and the condenser 108, and the resulting liquid refrigerant 120 is stored within the accumulator 110, as discussed with respect to Fig. 1.

[0063] It is to be understood that the process flow diagram of Fig. 2 is not intended to indicate that the two stage refrigeration system 200 is to include all the components shown in Fig. 2. Further, the two stage refrigeration system 200 may include any number of additional components not shown in Fig. 2, depending on the details of the specific implementation. For example, the two stage refrigeration system 200 may include any number of additional economizers or other types of equipment not shown in Fig. 2. In addition, the economizer 202 may be a heat exchange economizer rather than a flash tank. The heat exchange economizer may also be used to decrease refrigeration circulation rate and reduce compressor power usage.

[0064] In some embodiments, the two stage refrigeration system 200 includes more than one economizer 202, as well

as more than two compressors 210 and 212. For example, the two stage refrigeration system 200 may include two economizers and three compressors. In general, if the refrigeration system 200 includes X number of economizers, the refrigeration system 200 will include X + 1 number of compressors. Such a refrigeration system 200 with multiple economizers may form part of a cascade refrigeration system.

[0065] Fig. 3 is a process flow diagram of a single stage refrigeration system 300 including a heat exchanger economizer 302. Like numbered items are as described with respect to Fig. 1. In various embodiments, the single stage refrigeration system 300 utilizes a mixed fluorocarbon refrigerant. Further, in various embodiments, the single stage refrigeration system 300 is implemented upstream of a nitrogen refrigeration system or methane autorefrigeration system including an NRU. Multiple single stage refrigeration systems 300 may also be implemented in series upstream of such a nitrogen refrigeration system or methane autorefrigeration system.

[0066] As shown in Fig. 3, the saturated liquid refrigerant 112 leaving the accumulator 110 may be expanded across the expansion device 102 to an intermediate pressure at which vapor and liquid may be separated, producing the refrigerant mixture 114. The refrigerant mixture 114 may be flowed into the chiller 104 at a temperature lower than the temperature to which the process stream 116 is to be cooled. The process stream 116 may be cooled within the chiller 104, as discussed with respect to Fig. 1.

[0067] From the chiller 104, the saturated vapor refrigerant 118 may be flowed through the heat exchanger economizer 302. The cold, low-pressure saturated vapor refrigerant 118 may be used to subcool the saturated liquid refrigerant 112 within the heat exchanger economizer 302. The superheated vapor refrigerant 304 exiting the heat exchanger economizer 302 may then be flowed through the compressor 106 and the condenser 108, and the resulting liquid refrigerant 120 may be stored within the accumulator 110, as discussed with respect to Fig. 1.

[0068] It is to be understood that the process flow diagram of Fig. 3 is not intended to indicate that the single stage refrigeration system 300 is to include all the components shown in Fig. 3. Further, the single stage refrigeration system 300 may include any number of additional components not shown in Fig. 3, depending on the details of the specific implementation.

[0069] Fig. 4 is a process flow diagram of an LNG production system 400. As shown in Fig. 4, LNG 402 may be produced from a natural gas stream 404 using a number of different refrigeration systems. As shown in Fig. 4, a portion of the natural gas stream 404 may be separated from the natural gas stream 404 prior to entry into the LNG production system 400, and may be used as a fuel gas stream 406. The remaining natural gas stream 404 may be flowed into an initial natural gas processing system 408. Within the natural gas processing system 408, the natural gas stream 404 may be purified and cooled. For example, the natural gas stream 404 may be cooled using a first mixed fluorocarbon refrigerant 410, a second mixed fluorocarbon refrigerant 412, and a high-pressure nitrogen refrigerant 414. The cooling of the natural gas stream 404 may result in the production of the LNG 402. In some embodiments, the broader temperature range of a mixed refrigerant system will make it possible to use a single mixed refrigerant for both the first mixed fluorocarbon refrigerant 410 and the second mixed fluorocarbon refrigerant 412.

[0070] Within the LNG production system 400, heavy hydrocarbons 416 may be removed from the natural gas stream 406, and a portion of the heavy hydrocarbons 416 may be used to produce gasoline 418 within a heavy hydrocarbon processing system 420. In addition, any residual natural gas 422 that is separated from the heavy hydrocarbons 416 during the production of the gasoline 418 may be returned to the natural gas stream 404.

[0071] The produced LNG 402 may include some amount of nitrogen 424. Therefore, the LNG 402 may be flowed through an NRU 426. The NRU 426 separates the nitrogen 424 from the LNG 402, producing the final LNG product.

[0072] It is to be understood that the process flow diagram of Fig. 4 is not intended to indicate that the LNG production system 400 is to include all the components shown in Fig. 4. Further, the LNG production system 400 may include any number of additional components not shown in Fig. 4 or different locations for the fluorocarbon refrigerant chillers within the process, depending on the details of the specific implementation. For example, any number of alternative refrigeration systems may also be used to produce the LNG 402 from the natural gas stream 404. In addition, any number of different refrigeration systems may be used in combination to produce the LNG 402.

Hydrocarbon Processing Systems for the Production of LNG

[0073] According to embodiments described herein, LNG may be produced within a hydrocarbon processing system using mixed fluorocarbon refrigerants. In some embodiments, the fluorocarbon components within the mixed fluorocarbon refrigerants are non-flammable, non-toxic, and non-reactive. The fluorocarbon components for a particular mixed fluorocarbon refrigerant may be selected such that the cooling curve of the mixed fluorocarbon refrigerant closely matches the cooling curve of the LNG being chilled. Matching the cooling curve of the mixed fluorocarbon refrigerant to the cooling curve of the LNG may increase the performance and efficiency of the hydrocarbon processing system.

[0074] Fig. 5 is a process flow diagram of a hydrocarbon processing system 500 including an SMR cycle 502. The SMR cycle 502 may cool a feed gas 504 to produce LNG 506 using a mixed fluorocarbon refrigerant 508. The hydrocarbon processing system 500 also includes a low pressure NRU 510, which may be used to purify the LNG 506 by separating

the LNG 506 from a fuel stream 512 including nitrogen.

[0075] The SMR cycle 502 includes a heat exchanger 514, a compressor 516, a condenser 518, and an expansion device 520. The expansion device 520 may be an expansion valve or a hydraulic expander, for example. The mixed fluorocarbon refrigerant 508 is flowed from the condenser 518 to the heat exchanger 514. Within the heat exchanger

514, the mixed fluorocarbon refrigerant 508 cools the feed gas 504 to produce the LNG 506 via indirect heat exchange. **[0076]** From the heat exchanger 514, the mixed fluorocarbon refrigerant 508 is flowed to the expansion device 520, and is expanded across the expansion device 520 isenthalpically. On expansion, some vaporization occurs, creating a chilled mixed fluorocarbon refrigerant 522 that includes both vapor and liquid. The chilled mixed fluorocarbon refrigerant 522 is flowed back to the heat exchanger 514 and is used to aid in the cooling of the feed gas 508 within the heat exchanger 514. As the feed gas 508 exchanges heat with the chilled mixed fluorocarbon refrigerant 522, the chilled mixed fluorocarbon refrigerant 522 vaporizes, creating a vapor mixed fluorocarbon refrigerant 524.

[0077] The vapor mixed fluorocarbon refrigerant 524 is then compressed within the compressor 516 and flowed into the condenser 518. Within the condenser 518, the vapor mixed fluorocarbon refrigerant 524 is converted to a saturated, or slightly sub-cooled, liquid mixed fluorocarbon refrigerant 508. The liquid mixed fluorocarbon refrigerant 508 is then flowed back into the heat exchanger 514.

[0078] In various embodiments, the LNG 506 that is produced via the SMR cycle 502 includes some amount of impurities, such as nitrogen. Therefore, the LNG 506 is flowed to into the NRU 510. The NRU 510 separates the fuel stream 512 including the nitrogen from the LNG 506, producing the final LNG product. The final LNG product may then be flowed from the hydrocarbon processing system 500 to a desired destination using a pump 526.

[0079] It is to be understood that the process flow diagram of Fig. 5 is not intended to indicate that the hydrocarbon processing system 500 is to include all the components shown in Fig. 5. Further, the hydrocarbon processing system 500 may include any number of additional components not shown in Fig. 5, depending on the details of the specific implementation.

[0080] Fig. 6 is a process flow diagram of the hydrocarbon processing system 500 of Fig. 5 with the addition of a nitrogen refrigeration system 600. Like numbered items are as described with respect to Fig. 5. According to the embodiment shown in Fig. 6, the SMR cycle 502 may be operated at a higher temperature. Therefore, the output of the SMR cycle 502 may be cooled feed gas 504, rather than LNG 506, or may be a mixture of cooled feed gas 504 and LNG 506.

[0081] From the SMR cycle 502, the feed gas 504 is flowed into the nitrogen refrigeration system 600. Within the nitrogen refrigeration system 600, the feed gas may be cooled to produce the LNG 506 via indirect heat exchange with a nitrogen refrigerant 602 within a first heat exchanger 604. The LNG 506 is then flowed into the NRU 510, as discussed with respect to Fig. 5.

[0082] The nitrogen refrigeration system 600 includes the first heat exchanger 604, a second heat exchanger 606, a compressor 608, a condenser 610, and an expander 612. From the first heat exchanger 604, the nitrogen refrigerant 602 is flowed through the second heat exchanger 606. Within the second heat exchanger 606, the nitrogen refrigerant 602 is cooled via indirect heat exchange with a chilled, vapor nitrogen refrigerant 614. The nitrogen refrigerant 602 is then compressed within the compressor 608 and flowed into the condenser 610.

[0083] Within the condenser 610, the nitrogen refrigerant 602 is converted to the vapor nitrogen refrigerant 614. The vapor nitrogen refrigerant 614 is flowed through the second heat exchanger 606, in which the vapor nitrogen refrigerant 614 exchanges heat with the warmer nitrogen refrigerant 602 exiting the first heat exchanger 604.

[0084] The chilled, vapor nitrogen refrigerant 614 is then flowed through the expander 612. The expander 612 expands the vapor nitrogen refrigerant 614 to a low pressure with a corresponding reduction in temperature. The resulting cold nitrogen refrigerant 602 is flowed through the first heat exchanger 604 to exchange heat with the feed gas 504.

[0085] It is to be understood that the process flow diagram of Fig. 6 is not intended to indicate that the hydrocarbon processing system 600 is to include all the components shown in Fig. 6. Further, the hydrocarbon processing system 600 may include any number of additional components not shown in Fig. 6, depending on the details of the specific implementation.

[0086] Fig. 7 is a process flow diagram of the hydrocarbon processing system 500 of Fig. 5 with the addition of a methane autorefrigeration system 700. Like numbered items are as described with respect to Fig. 5. According to the embodiment shown in Fig. 7, the SMR cycle 502 may be operated at a higher temperature. Therefore, the output of the SMR cycle 502 may be cooled feed gas 504, rather than LNG 506, or may be a mixture of cooled feed gas 504 and LNG 506.

[0087] From the SMR cycle 502, the cooled feed gas 504 is flowed into the NRU 510. The NRU 510 purifies the feed gas 504, producing an LNG bottoms stream 702 and a fuel gas overhead stream 704. The LNG bottoms stream 702 is flowed through an expansion device 706, such as an expansion valve or hydraulic expander, and into a heat exchanger 708. Within the heat exchanger 708, the LNG bottoms stream 702 exchanges heat with the overhead fuel stream 704, cooling the overhead fuel stream 704 and producing a mixed fuel stream 710 including both the vapor fuel stream 512 and a liquid fuel stream 712.

[0088] The mixed fuel stream 710 is then flowed into a flash drum 714. The flash drum 714 separates the vapor fuel stream 512 from the liquid fuel stream 712. The liquid fuel stream 712 may then be flowed back into the NRU 510 as reflux.

[0089] As the LNG bottoms stream 702 exchanges heat with the overhead fuel stream 704 within the heat exchanger 708, it may be partially vaporized, producing a mixed phase feed stream 716. From the heat exchanger 708, the mixed phase feed stream 716 is flowed into a first flash drum 718 within the methane autorefrigeration system 700.

[0090] The first flash drum 718 separates the mixed phase feed stream 716 into a vapor stream 720 that includes primarily natural gas and an LNG stream 722. The vapor stream 720 is flowed into a first compressor 724. From the first compressor 724, the resulting natural gas stream 726 may be combined with the initial feed gas 504 prior to entry of the feed gas 504 into the SMR cycle 502.

[0091] From the first flash drum 718, the LNG stream 722 is flowed through an expansion device 728, such as an expansion valve or hydraulic expander, which may control the flow of the LNG stream 728 into a second flash drum 730. Specifically, the expansion device 728 may allow a portion of the liquid from the LNG stream 722 to flash, creating a mixed phase stream that is flowed into the second flash drum 730.

[0092] The second flash drum 730 separates the mixed phase stream into the final LNG product 506 and a vapor stream 732 that includes primarily natural gas. The vapor stream 732 is flowed into a second compressor 734. From the second compressor 734, the vapor stream 732 is combined with the vapor stream 720 from the first flash drum 718 prior to entry of the vapor stream 720 into the first compressor 724. Furthermore, from the second flash drum 730, the final LNG product 506 may be flowed to a desired destination using the pump 526.

[0093] It is to be understood that the process flow diagram of Fig. 7 is not intended to indicate that the hydrocarbon processing system 700 is to include all the components shown in Fig. 7. Further, the hydrocarbon processing system 700 may include any number of additional components not shown in Fig. 7, depending on the details of the specific implementation.

[0094] Fig. 8 is a process flow diagram of a hydrocarbon processing system 800 including a pre-cooled SMR cycle 802. The pre-cooled SMR cycle 802 may cool a feed gas 804 to produce LNG 806 using a mixed fluorocarbon refrigerant 808. The hydrocarbon processing system 800 also includes a low pressure NRU 810, which may be used to purify the LNG 806 by separating the LNG 806 from a fuel stream 812 including nitrogen.

[0095] Within the pre-cooled SMR cycle 802, the incoming feed gas 804 is pre-cooled and partially condensed in a first chiller 814 via indirect heat exchange with a fluorocarbon refrigerant. For example, the feed gas 804 may be cooled in the first chiller 814 using a refrigerant blend such as R-410a or R-404a, or using a pure component refrigerant such as R-125, R-32, or R-218.

[0096] The chilled feed gas 816 is then flowed into a main cryogenic heat exchanger 818. Within the main cryogenic heat exchanger 818, the feed gas 816 is cooled to produce the LNG 806 via indirect heat exchange with the mixed fluorocarbon refrigerant 808. The main cryogenic heat exchanger 818 may include a number of small-diameter, spiral-wound tube bundles 820, which may permit very close temperature matches between the chilled feed gas 816 and the mixed fluorocarbon refrigerant 808.

[0097] After the mixed fluorocarbon refrigerant 808 flows through the main cryogenic heat exchanger 818, the mixed fluorocarbon refrigerant 808 is expanded across an expansion device 822, such as an expansion valve or hydraulic expander. On expansion, some vaporization occurs, creating a chilled mixed fluorocarbon refrigerant 824 that includes both vapor and liquid. The chilled mixed fluorocarbon refrigerant 824 is then sprayed into the main cryogenic heat exchanger 818 via a number of spray nozzles 826. In various embodiments, spraying the chilled mixed fluorocarbon refrigerant 824 into the main cryogenic heat exchanger 818 provides for additional cooling of the feed gas 816 and the mixed fluorocarbon refrigerant 808 flowing through the tube bundles 820.

[0098] The chilled mixed fluorocarbon refrigerant 824 is then flowed out of the main cryogenic heat exchanger 818 as a bottoms stream 828. The bottoms stream 828 is compressed in a compressor 830, producing a compressed mixed fluorocarbon refrigerant 832. The compressed mixed fluorocarbon refrigerant 832 is chilled and partially condensed within a second chiller 834 and a third chiller 836. The resulting chilled mixed fluorocarbon refrigerant 838 is flowed into a flash drum 839, which separates the chilled mixed fluorocarbon refrigerant 838 into a vapor stream and a liquid stream. The vapor stream is flowed into the main cryogenic heat exchanger 818 as the mixed fluorocarbon refrigerant 808, and the liquid stream is flowed into the main cryogenic heat exchanger 818 as an additional mixed fluorocarbon refrigerant 840. The additional mixed fluorocarbon refrigerant 840 may provide cooling for the mixed fluorocarbon refrigerant 808 via indirect heat exchange with the mixed fluorocarbon refrigerant 808.

[0099] Upon exiting the main cryogenic heat exchanger 818, the additional mixed fluorocarbon refrigerant 840 is expanded across an expansion device 842, such as an expansion valve or hydraulic expander. On expansion, some vaporization occurs, creating a chilled mixed fluorocarbon refrigerant 844 that includes both vapor and liquid. The chilled mixed fluorocarbon refrigerant 844 is then sprayed into the main cryogenic heat exchanger 818 via a number of additional spray nozzles 846. After flowing through the main cryogenic heat exchanger 818, the chilled mixed fluorocarbon refrigerant 844 is flowed out of the main cryogenic heat exchanger 818 along with the bottoms stream 828.

[0100] From the main cryogenic heat exchanger 818, the produced LNG 806 is flowed through an expansion device

848, such as an expansion valve or hydraulic expander, and into the NRU 810. The NRU 810 separates the fuel stream 812 from the LNG 806, producing the final LNG product. The final LNG product may then be flowed from the hydrocarbon processing system 800 to a desired destination using a pump 850.

[0101] It is to be understood that the process flow diagram of Fig. 8 is not intended to indicate that the hydrocarbon processing system 800 is to include all the components shown in Fig. 8. Further, the hydrocarbon processing system 800 may include any number of additional components not shown in Fig. 8, depending on the details of the specific implementation. In some embodiments, the mixed fluorocarbon refrigerant 808 used in the main cryogenic heat exchanger 818 of Fig. 8 includes nitrogen, *e.g.*, R-728, and/or argon, *e.g.*, R-740, in addition to one or more fluorocarbon refrigerant components.

[0102] Fig. 9 is a process flow diagram of a hydrocarbon processing system 900 including a DMR cycle 902. The DMR cycle 902 may include a warm MR cycle and a cold MR cycle connected in series. The DMR cycle 902 may be used to cool a feed gas 904 to produce LNG 906 using a first mixed fluorocarbon refrigerant 908 within the warm MR cycle and a second mixed fluorocarbon refrigerant 910 within the cold MR cycle. The hydrocarbon processing system 900 also includes a low pressure NRU 912, which may be used to purify the LNG 906 by separating the LNG 906 from a fuel stream 914 including nitrogen.

[0103] In some embodiments, the first mixed fluorocarbon refrigerant 908 within the warm MR cycle includes R-32, R-152a, R-245fa, R-227ea, HFE-347mcc, and/or other high boiling components. In addition, in some embodiments, the second mixed fluorocarbon refrigerant 910 within the cold MR cycle includes R-14, R-170, R-41, xenon, R-23, R-116, R-1150, R-50, R-784, and/or other low boiling components.

[0104] Within the hydrocarbon processing system 900, the feed gas 904 is cooled to produce the LNG 906 using a first heat exchanger 916 and a second heat exchanger 918. The feed gas 904 is cooled within the first heat exchanger 916 via indirect heat exchange along with the first mixed fluorocarbon refrigerant 908 and the second mixed fluorocarbon refrigerant 910.

[0105] From the first heat exchanger 916, the first mixed fluorocarbon refrigerant 908 is flowed to an expansion device 920, such as an expansion valve or hydraulic expander, and is expanded across the expansion device 920 isenthalpically. On expansion, some vaporization occurs, creating a chilled mixed fluorocarbon refrigerant 922 that includes both vapor and liquid. The chilled mixed fluorocarbon refrigerant 922 is flowed back to the first heat exchanger 916 and is used to cool the first mixed fluorocarbon refrigerant 908, the second mixed fluorocarbon refrigerant 910, and the feed gas 904 within the first heat exchanger 916. As the first mixed fluorocarbon refrigerant 908, the second mixed fluorocarbon refrigerant 910, and the feed gas 904 exchange heat with the chilled mixed fluorocarbon refrigerant 922, the chilled mixed fluorocarbon refrigerant 922 vaporizes, creating a vapor mixed fluorocarbon refrigerant 924.

[0106] The vapor mixed fluorocarbon refrigerant 924 is then compressed within a compressor 926 and condensed within a condenser 928. The condensed mixed fluorocarbon refrigerant is then flowed back into the first heat exchanger 916 as the first mixed fluorocarbon refrigerant 908.

[0107] From the first heat exchanger 916, the second mixed fluorocarbon refrigerant 910 is flowed into the second heat exchanger 918. Within the second heat exchanger 918, the second mixed fluorocarbon refrigerant 910 is further cooled along with the feed gas 904, producing the LNG 906.

[0108] Upon exiting the second heat exchanger 918, the second mixed fluorocarbon refrigerant 910 is flowed to an expansion device 930, such as an expansion valve or hydraulic expander, and is expanded across the expansion device 930 isenthalpically. On expansion, some vaporization occurs, creating a chilled mixed fluorocarbon refrigerant 932 that includes both vapor and liquid. The chilled mixed fluorocarbon refrigerant 932 is flowed back to the second heat exchanger 918 and is used to cool both the feed gas 904 and the second mixed fluorocarbon refrigerant 910 within the second heat exchanger 918. As the feed gas 904 exchanges heat with the chilled mixed fluorocarbon refrigerant 932, the chilled mixed fluorocarbon refrigerant 932 vaporizes, creating a vapor mixed fluorocarbon refrigerant 934.

[0109] The vapor mixed fluorocarbon refrigerant 934 is then compressed within a compressor 936, and cooled within a heat exchanger 938. The condensed mixed fluorocarbon refrigerant is flowed back into the first heat exchanger 916 as the second mixed fluorocarbon refrigerant 910.

[0110] In various embodiments, the LNG 906 that is produced via the DMR cycle 902 includes some amount of impurities, such as nitrogen. Therefore, the LNG 906 is flowed to into the NRU 912. The NRU 912 separates the fuel stream 914 from the LNG 906, producing the final LNG product. The final LNG product may be flowed from the hydrocarbon processing system 900 to a desired destination using a pump 940.

[0111] It is to be understood that the process flow diagram of Fig. 9 is not intended to indicate that the hydrocarbon processing system 900 is to include all the components shown in Fig. 9. Further, the hydrocarbon processing system 900 may include any number of additional components not shown in Fig. 9, depending on the details of the specific implementation.

[0112] Figs. 10A and 10B are process flow diagrams of a hydrocarbon processing system 1000 including an SMR cycle 1002, an NRU 1004, and a methane autorefrigeration system 1006. In various embodiments, the hydrocarbon processing system 1000 is used to produce LNG 1008 from a natural gas stream 1010.

[0113] As shown in Fig. 10A, the natural gas stream 1010 is flowed into a pipe joint 1012 within the hydrocarbon processing system 1000. The pipe joint 1012 combines the natural gas stream 1010 with another natural gas stream. The combined natural gas stream is compressed within a first compressor 1014 and flowed into another pipe joint 1016 via line 1018.

[0114] The pipe joint 1016 splits the natural gas stream into two separate natural gas streams. A first natural gas stream is combined with another natural gas stream via a pipe joint 1020 and then flowed out of the hydrocarbon processing system 1000 as fuel 1022. A second natural gas stream is chilled within a first chiller 1024 and flowed into another pipe joint 1026. The pipe joint 1026 splits the natural gas stream into two separate natural gas streams. A first natural gas stream is flowed into a first heat exchanger 1028 within the SMR cycle 1002 via line 1030. A second natural gas stream is flowed into a second heat exchanger 1032 via line 1034.

[0115] Within the first heat exchanger 1028, the natural gas stream is cooled via indirect heat exchange with a circulating mixed fluorocarbon refrigerant stream. From the first heat exchanger 1028, the mixed fluorocarbon refrigerant stream is flowed to an expansion device 1036, such as an expansion valve or hydraulic expander, via line 1038, and is expanded across the expansion device 1036 isenthalpically. On expansion, some vaporization occurs, creating a chilled mixed fluorocarbon refrigerant stream that includes both vapor and liquid. The chilled mixed fluorocarbon refrigerant stream is flowed back to the first heat exchanger 1028 and is used to aid in the cooling of the natural gas stream within the first heat exchanger 1028. As the natural gas stream exchanges heat with the chilled mixed fluorocarbon refrigerant stream, the chilled mixed fluorocarbon refrigerant stream vaporizes, creating a vapor mixed fluorocarbon refrigerant stream.

[0116] The vapor mixed fluorocarbon refrigerant is then compressed within a second compressor 1040 and partially condensed within a second chiller 1042. The condensed mixed fluorocarbon refrigerant is then flowed into a first flash drum 1044 via line 1046. The flash drum separates the partially condensed mixed fluorocarbon refrigerant stream into a vapor mixed fluorocarbon refrigerant stream and a liquid mixed fluorocarbon refrigerant. The vapor mixed fluorocarbon refrigerant stream is compressed within a third compressor 1048 and flowed into a pipe joint 1050. The liquid mixed fluorocarbon refrigerant stream is pumped into the pipe joint 1050 via a pump 1052.

[0117] Within the pipe joint 1050, the vapor and liquid mixed fluorocarbon refrigerant streams are recombined. The recombined mixed fluorocarbon refrigerant stream is further cooled within a third chiller 1053 and flowed back into the first heat exchanger 1028. Within the first heat exchanger 1028, the recombined mixed fluorocarbon refrigerant stream is fully condensed and sub-cooled, and is then flowed back to the expansion device 1036 via line 1038.

[0118] From the first heat exchanger 1028, the resulting LNG stream is flowed into a pipe joint 1054, in which it is combined with an LNG stream from the second heat exchanger 1032. The combined LNG stream is then flowed into the NRU 1004 via line 1056 to remove excess nitrogen from the LNG stream. Specifically, the LNG stream is flowed into a reboiler 1058, which decreases the temperature of the LNG stream. The cooled LNG stream may be expanded within a hydraulic expansion turbine 1060 and flowed through an expansion device 1062, such as an expansion valve or hydraulic expander, which lowers the temperature and pressure of the LNG stream.

[0119] The LNG stream is flowed into a cryogenic fractionation column 1064, such as an NRU tower, within the NRU 1004. In addition, heat is transferred to the cryogenic fractionation column 1064 from the reboiler 1058 via line 1066. The cryogenic fractionation column 1064 separates nitrogen from the LNG stream via a cryogenic distillation process. An overhead stream is flowed out of the cryogenic fractionation column 1064 via line 1068. The overhead stream may include primarily methane, nitrogen, and other low boiling point or non-condensable gases, such as helium, which have been separated from the LNG stream.

[0120] The overhead stream is flowed into a reflux condenser 1070 via line 1068. Within the reflux condenser 1070, the overhead stream is cooled via indirect heat exchange with an LNG stream. The heated overhead stream is then flowed into a reflux separator 1072. The reflux separator 1072 separates any liquid within the overhead stream and returns the liquid to the cryogenic fractionation column 1064 as reflux. The separation of the liquid from the overhead stream via the reflux separator 1072 results in the production of a vapor stream. The vapor stream may be a fuel stream including primarily nitrogen and other low boiling point gases. From the reflux separator 1072, the vapor stream is flowed through the second heat exchanger 1032 via line 1074. The vapor stream is compressed within a fourth compressor 1076, chilled within a fourth chiller 1078, further compressed within a fifth compressor 180, and further chilled within a fifth chiller 1082. The fuel stream is then combined with the other natural gas stream within the pipe joint 1020 and flowed out of the hydrocarbon processing system 1000 as fuel 1022.

[0121] The bottoms stream that is produced within the cryogenic fractionation column 1064 includes primarily LNG with traces of nitrogen. The LNG stream is flowed into the reflux condenser 1070 and is used to cool the overhead stream from the cryogenic fractionation column 1064. As the LNG stream exchanges heat with overhead stream, it is partially vaporized, producing a multiphase natural gas stream.

[0122] The multiphase natural gas stream is flowed into a second flash drum 1084 via line 1083. The second flash drum 1084 separates the multiphase natural gas stream into a natural gas stream and an LNG stream. The natural gas stream is combined within another natural gas stream within a pipe joint 1086, compressed within a sixth compressor 1087, and combined with the initial natural gas stream 1010 within the pipe joint 1012.

[0123] From the second flash drum 1084, the LNG stream is flowed through an expansion device 1088, such as an expansion valve or hydraulic expander, that controls the flow of the natural gas stream into a third flash drum 1089. The expansion device 1088 reduces the temperature and pressure of the natural gas stream, resulting in the flash evaporation of the natural gas stream into both a natural gas stream and an LNG stream. The natural gas stream is then separated

from the LNG steam via the third flash drum 1089.

[0124] The natural gas stream is flowed from the third flash drum 1089 into a pipe joint 1090, in which the natural gas stream is combined with another natural gas stream. The combined natural gas stream is compressed within a seventh compressor 1091 and then flowed into the pipe joint 1086.

[0125] From the third flash drum 1089, the LNG stream is flowed through an expansion device 1092, such as an expansion valve or hydraulic expander, that controls the flow of the natural gas stream into a fourth flash drum 1093. The expansion device 1092 reduces the temperature and pressure of the natural gas stream, resulting in the flash evaporation of the natural gas stream into both a natural gas stream and an LNG stream. The natural gas stream is then separated from the LNG steam via the fourth flash drum 1093.

[0126] The natural gas stream is flowed from the fourth flash drum 1093 into a pipe joint 1094, in which the natural gas stream is combined with another natural gas stream. The combined natural gas stream is compressed within an eighth compressor 1095 and flowed into the pipe joint 1090.

[0127] The LNG stream is flowed into an LNG tank 1096. The LNG tank 1096 may store the LNG stream for any period of time. Boil-off gas generated within the LNG tank 1096 is flowed to the pipe joint 1094 and combined within the natural gas stream from the fourth flash drum 1093. At any point in time, the final LNG stream 1008 may be transported to a LNG tanker 1097 using a pump 1098, for transport to markets. Additional boil-off gas 1099 generated while loading the final LNG stream 1008 into the LNG tanker 1097 may be recovered in the hydrocarbon processing system 1000.

[0128] It is to be understood that the process flow diagrams of Figs. 10A and 10B are not intended to indicate that the hydrocarbon processing system 1000 is to include all the components shown in Figs. 10A and 10B. Further, the hydrocarbon processing system 1000 may include any number of additional components not shown in Figs. 10A and 10B, depending on the details of the specific implementation.

[0129] Figs. 11A and 11B are process flow diagrams of a hydrocarbon processing system 1100 including an economized DMR cycle 1102, an NRU 1104, and a methane autorefrigeration system 1106. In various embodiments, the hydrocarbon processing system 1100 is used to produce LNG 1108 from a natural gas stream 1110.

[0130] As shown in Fig. 11A, the natural gas stream 1110 is flowed into a pipe joint 1112 within the hydrocarbon processing system 1100. The pipe joint 1112 splits the natural gas stream 1110 into three separate natural gas streams. A first natural gas stream is flowed to a pipe joint 1114 via line 1116. Within the pipe joint 1114, the first natural gas stream is combined with another stream including natural gas, and the combined stream is flowed out of the hydrocarbon processing system 1100 as fuel 1118.

[0131] From the pipe joint 1112, a second natural gas stream is flowed into the NRU 1104. Within the NRU 1104, the natural gas stream is cooled within a first heat exchanger 1120 and combined with an LNG stream exiting the economized DMR cycle 1102 within a pipe joint 1122.

[0132] Furthermore, a third natural gas stream is flowed from the pipe joint 1112 to another pipe joint 1124 as the main feed stream. Within the pipe joint 1124, the natural gas stream is combined with another natural gas stream from the methane autorefrigeration system 1106. The combined natural gas stream is then cooled within the economized DMR cycle 1102. Specifically, the natural gas stream is cooled using a second heat exchanger 1126, a third heat exchanger 1128, and a fourth heat exchanger 1130 within a warm MR cycle of the economized DMR cycle 1102. The natural gas stream is further cooled using a fifth heat exchanger 1132 and a sixth heat exchanger 1134 within a cold MR cycle of the economized DMR cycle 1102.

[0133] Within the second heat exchanger 1126, the natural gas stream is cooled via indirect heat exchange with a circulating warm fluorocarbon refrigerant stream. From the second heat exchanger 1126, the warm fluorocarbon refrigerant stream is flowed into a pipe joint 1140, in which it is combined with another warm fluorocarbon refrigerant stream from the third and fourth heat exchangers 1128 and 1130.

[0134] From the pipe joint 1140, the warm fluorocarbon refrigerant stream is compressed within a compressor 1142 and chilled within a chiller 1144. The warm fluorocarbon refrigerant stream is then flowed through the second heat exchanger 1126. Within the second heat exchanger 1126, the warm fluorocarbon refrigerant stream is sub-cooled via indirect heat exchange. From the second heat exchanger 1126, the sub-cooled fluorocarbon refrigerant stream is flowed to a pipe joint 1148, which splits the fluorocarbon refrigerant stream into two fluorocarbon refrigerant streams. A first fluorocarbon refrigerant stream is flowed through an expansion device 1150 and back into the second heat exchanger 1126. Within the second heat exchanger 1126, the fluorocarbon refrigerant stream cools the natural gas stream and the other fluorocarbon refrigerant streams flowing through the second heat exchanger 1126. The fluorocarbon refrigerant stream is then flowed into the pipe joint 1140.

[0135] A second fluorocarbon refrigerant stream is flowed from the pipe joint 1150 into the third heat exchanger 1128 via line 1152. Within the third heat exchanger 1128, the fluorocarbon refrigerant stream is further chilled and sub-cooled

via indirect heat exchange. From the third heat exchanger 1128, the sub-cooled fluorocarbon refrigerant stream is flowed to a pipe joint 1153, which splits the fluorocarbon refrigerant stream into two fluorocarbon refrigerant streams. A first fluorocarbon refrigerant stream is flowed through an expansion device 1154 and back into the third heat exchanger 1128. Within the third heat exchanger 1128, the fluorocarbon refrigerant stream cools the natural gas stream and the other fluorocarbon refrigerant streams flowing through the third heat exchanger 1128. The fluorocarbon refrigerant stream is then flowed into a pipe joint 1156, in which it is combined with another warm fluorocarbon refrigerant stream from the fourth heat exchanger 1130. From the pipe joint 1156, the combined warm fluorocarbon refrigerant stream is compressed within a compressor 1158, chilled within a chiller 1159, and flowed into the pipe joint 1140 to be combined with the fluorocarbon refrigerant stream exiting the second heat exchanger 1126.

[0136] A second fluorocarbon refrigerant stream is flowed from the pipe joint 1153 into the fourth heat exchanger 1130 via line 1160. Within the fourth heat exchanger 1130, the fluorocarbon refrigerant stream is further chilled and sub-cooled via indirect heat exchange. From the fourth heat exchanger 1130, the sub-cooled fluorocarbon refrigerant stream is flowed through an expansion device 1161 and back into the fourth heat exchanger 1130. Within the fourth heat exchanger 1130, the fluorocarbon refrigerant stream cools the natural gas stream and the other fluorocarbon refrigerant streams flowing through the fourth heat exchanger 1130. The fluorocarbon refrigerant stream is then compressed within a compressor 1163 and flowed into the pipe joint 1156 to be combined with the fluorocarbon refrigerant stream exiting the third heat exchanger 1128.

[0137] In various embodiments, a fluorocarbon refrigerant stream from the cold MR cycle of the economized DMR cycle 1102 is flowed through the second heat exchanger 1126, the third heat exchanger 1128, and the fourth heat exchanger 1130 within the warm MR cycle via line 1164. Within the second heat exchanger 1126, the third heat exchanger 1128, and the fourth heat exchanger 1130, the fluorocarbon refrigerant stream from the cold MR cycle is cooled and condensed via indirect heat exchange with the fluorocarbon refrigerant within the warm MR cycle. The cold, liquid fluorocarbon refrigerant stream exiting the fourth heat exchanger 1130 is flowed into the fifth heat exchanger 1132 of the cold MR cycle via line 1165.

[0138] Within the fifth heat exchanger 1132, the cold fluorocarbon refrigerant stream is further sub-cooled via indirect heat exchange. From the fifth heat exchanger 1132, the sub-cooled fluorocarbon refrigerant stream is flowed to a pipe joint 1166, which splits the fluorocarbon refrigerant stream into two fluorocarbon refrigerant streams. A first fluorocarbon refrigerant stream is flowed through an expansion device 1167 and back into the fifth heat exchanger 1132. Within the fifth heat exchanger 1132, the fluorocarbon refrigerant stream cools the natural gas stream and the incoming liquid fluorocarbon refrigerant stream 1165. The fluorocarbon refrigerant stream is then flowed into a pipe joint 1168, in which it is combined with a fluorocarbon refrigerant stream from the sixth heat exchanger 1134. The combined fluorocarbon refrigerant stream is compressed within a compressor 1169, chilled within a chiller 1170, and flowed back into the warm MR cycle of economized DMR cycle 1102 via line 1164.

[0139] A second fluorocarbon refrigerant stream is flowed from the pipe joint 1166 into the sixth heat exchanger 1134 via line 1171. Within the sixth heat exchanger 1134, the fluorocarbon refrigerant stream is further chilled and sub-cooled via indirect heat exchange. From the sixth heat exchanger 1134, the fluorocarbon refrigerant stream is flowed through an expansion valve 1172 and back into the sixth heat exchanger 1134. Within the sixth heat exchanger 1134, the fluorocarbon refrigerant stream cools the natural gas stream, producing an LNG stream, and chills the liquid fluorocarbon refrigerant stream. The fluorocarbon refrigerant stream is then compressed within a compressor 1173 and flowed into the pipe joint 1168, in which it is combined with the fluorocarbon refrigerant stream exiting the fifth heat exchanger 1132.

[0140] From the sixth heat exchanger 1134, the resulting LNG stream is flowed out of the economized DMR cycle 1102 and into the NRU 1104 via line 1174. Specifically, the LNG stream is flowed into the pipe joint 1122, in which it is combined with the natural gas stream exiting the first heat exchanger 1120. The LNG stream is then flowed into a reboiler 1175, which decreases the temperature of the LNG stream. The cooled LNG stream may be expanded within a hydraulic expansion turbine 1176 and flowed through an expansion device 1177, such as an expansion valve or hydraulic expander, which lowers the temperature and pressure of the LNG stream.

[0141] The LNG stream is flowed into a cryogenic fractionation column 1178, such as an NRU tower, within the NRU 1104. In addition, heat is transferred to the cryogenic fractionation column 1178 from the reboiler 1175 via line 1179. The cryogenic fractionation column 1178 separates nitrogen from the LNG stream via a cryogenic distillation process. An overhead stream is flowed out of the cryogenic fractionation column 1178 via line 1180. The overhead stream may include primarily methane, nitrogen, and other low boiling point or non-condensable gases, such as helium, which have been separated from the LNG stream.

[0142] The overhead stream is flowed into a reflux condenser 1181. Within the reflux condenser 1181, the overhead stream is cooled via indirect heat exchange with an LNG stream. The heated overhead stream is then flowed into a reflux separator 1182. The reflux separator 1182 separates any liquid within the overhead stream and returns the liquid to the cryogenic fractionation column 1178 as reflux. The separation of the liquid from the overhead stream via the reflux separator 1182 results in the production of a vapor stream. The vapor stream may be a fuel stream including primarily nitrogen and other low boiling point gases. From the reflux separator 1182, the vapor stream is flowed through the first

heat exchanger 1120. The vapor stream is then progressively compressed and chilled within a first compressor 1183, a first chiller 1184, a second compressor 1185, and a second chiller 1186. The compressed, chilled stream is then combined with a natural gas stream within the pipe joint 1114, and the combined stream is flowed out of the hydrocarbon processing system 1100 as fuel 1118.

[0143] The bottoms stream that is produced within the cryogenic fractionation column 1178 includes primarily LNG with traces of nitrogen. The LNG is flowed through the reflux condenser 1181 and is used to cool the overhead stream from the cryogenic fractionation column 1178. As the LNG stream exchanges heat with the overhead stream, it is partially vaporized, producing a multiphase natural gas stream.

[0144] The multiphase natural gas stream is flowed into a third flash drum 1187, which separates the multiphase natural gas stream into a natural gas stream and an LNG stream. The natural gas stream is combined within another natural gas stream within a pipe joint 1188, compressed within a compressor 1189, chilled within a chiller 1190, and combined with the initial natural gas stream within the pipe joint 1124.

[0145] From the third flash drum 1187, the LNG stream is flowed through an expansion device 1191, such as an expansion valve or hydraulic expander, that controls the flow of the natural gas stream into a fourth flash drum 1192. The expansion device 1191 reduces the temperature and pressure of the natural gas stream, resulting in the flash evaporation of the natural gas stream into both a natural gas stream and an LNG stream. The natural gas stream is then separated from the LNG stream via the fourth flash drum 1192.

[0146] The natural gas stream is flowed from the fourth flash drum 1192 into a pipe joint 1193, in which the natural gas stream is combined with another natural gas stream. The combined natural gas stream is compressed within a compressor 1194 and then flowed into the pipe joint 1188 to be combined with the natural gas stream from the third flash drum 1187.

[0147] From the fourth flash drum 1192, the LNG stream is flowed into an LNG tank 1195. The LNG tank 1195 may store the LNG stream for any period of time. Boil-off gas generated within the LNG tank 1195 is flowed to the pipe joint 1193 and combined within the natural gas stream from the fourth flash drum 1192. At any point in time, the final LNG stream 1108 may be transported to a LNG tanker 1196 using a pump 1197, for transport to markets. Additional boil-off gas 1198 generated while loading the final LNG stream 1108 into the LNG tanker 1196 may be recovered in the hydrocarbon processing system 1100.

Method for LNG Production

[0148] Fig. 12 is a process flow diagram of a method 1200 for the formation of LNG from a natural gas stream using a mixed fluorocarbon refrigerant. The method 1200 may be implemented within any suitable type of hydrocarbon processing system. For example, the method 1200 may be implemented by any of the hydrocarbon processing systems 500 or 800-1100 discussed with respect to Figs. 5-11.

[0149] The method 1200 begins at block 1202, at which a natural gas is cooled to produce LNG in a fluorocarbon refrigeration system using a mixed fluorocarbon refrigerant. The mixed fluorocarbon refrigerant may include any suitable mixture of fluorocarbon components, or any suitable mixture of fluorocarbon components and other non-flammable components, such as inert compounds. For example, the mixed fluorocarbon refrigerant may be a mixture of any number of different HFCs, HFOs, and/or inert compounds.

[0150] Cooling the natural gas in the fluorocarbon refrigeration system may include compressing the mixed fluorocarbon refrigerant to provide a compressed mixed fluorocarbon refrigerant and cooling the compressed mixed fluorocarbon refrigerant by indirect heat exchange with a cooling fluid to provide a cooled mixed fluorocarbon refrigerant. The cooled mixed fluorocarbon refrigerant may then be passed to a heat exchange area, and the natural gas may be cooled by indirect heat exchange with the cooled mixed fluorocarbon refrigerant in the heat exchange area.

[0151] The fluorocarbon refrigeration system may be any suitable type of refrigeration system that is capable of cooling a natural gas stream using a mixed fluorocarbon refrigerant. For example, the fluorocarbon refrigeration system may be an SMR cycle, DMR cycle, TMR cycle, or pre-cooled MR cycle. If the fluorocarbon refrigeration system is a DMR cycle, for example, the fluorocarbon refrigeration system may include a first MR cycle that uses a warm mixed fluorocarbon refrigerant and a second MR cycle that uses a cold mixed fluorocarbon refrigerant. The first mixed refrigerant cycle and the second mixed refrigerant cycle may be connected in series.

[0152] At block 1204, nitrogen is removed from the LNG in an NRU. In some embodiments, the nitrogen stream separated from the natural gas via the NRU is used to further cool at least a portion of the natural gas.

[0153] In various embodiments, the natural gas is further cooled to produce the LNG in an autorefrigeration system. The autorefrigeration system may include a number of expansion devices and flash drums for cooling the natural gas. In addition, in some embodiments, the natural gas is further cooled to produce the LNG in a nitrogen refrigeration system using a nitrogen refrigerant. The nitrogen refrigeration system may be located upstream of the autorefrigeration system, for example.

[0154] It is to be understood that the process flow diagram of Fig. 12 is not intended to indicate that the blocks of the

method 1200 are to be executed in any particular order, or that all of the blocks are to be included in every case. Further, any number of additional blocks may be included within the method 1200, depending on the details of the specific implementation.

5 Embodiments

[0155] Embodiments of the techniques may include any combinations of the methods and systems shown in the following numbered paragraphs. This is not to be considered a complete listing of all possible embodiments, as any number of variations can be envisioned from the description herein.

10 1. A hydrocarbon processing system for liquefied natural gas (LNG) production, including:

a fluorocarbon refrigeration system configured to cool a natural gas to produce LNG using a mixed fluorocarbon refrigerant; and

15 a nitrogen rejection unit (NRU) configured to remove nitrogen from the LNG.

20 2. The hydrocarbon processing system of paragraph 1, including a nitrogen refrigeration system configured to further cool the natural gas to produce the LNG using a nitrogen refrigerant.

3. The hydrocarbon processing system of any of paragraphs 1 or 2, including an autorefrigeration system configured to further cool the natural gas to produce the LNG.

25 4. The hydrocarbon processing system of paragraph 3, wherein the autorefrigeration system includes a number of flash drums and a number of expansion devices.

5. The hydrocarbon processing system of any of paragraphs 1-3, wherein at least a portion of the natural gas is cooled using a nitrogen stream separated from the natural gas via the NRU.

30 6. The hydrocarbon processing system of any of paragraphs 1-3 or 5, wherein the fluorocarbon refrigeration system includes a single mixed refrigerant cycle.

35 7. The hydrocarbon processing system of any of paragraphs 1-3, 5, or 6, wherein the fluorocarbon refrigeration system includes a pre-cooled mixed refrigerant cycle.

8. The hydrocarbon processing system of any of paragraphs 1-3 or 5-7, wherein the fluorocarbon refrigeration system includes a dual mixed refrigerant cycle.

40 9. The hydrocarbon processing system of paragraph 8, wherein the dual mixed refrigerant cycle includes:

a first mixed refrigerant cycle that uses a warm mixed fluorocarbon refrigerant; and

45 a second mixed refrigerant cycle that uses a cold mixed fluorocarbon refrigerant, wherein the first mixed refrigerant cycle and the second mixed refrigerant cycle are connected in series.

10. The hydrocarbon processing system of any of paragraphs 1-3 or 5-8, wherein the fluorocarbon refrigeration system includes a triple mixed refrigerant cycle.

50 11. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, or 10, wherein the fluorocarbon refrigeration system includes a heat exchanger configured to allow for cooling of the natural gas via an indirect exchange of heat between the natural gas and the mixed fluorocarbon refrigerant.

12. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, 10, or 11, wherein the fluorocarbon refrigeration system includes:

55 a compressor configured to compress the mixed fluorocarbon refrigerant to provide a compressed mixed fluorocarbon refrigerant;

a chiller configured to cool the compressed mixed fluorocarbon refrigerant to provide a cooled mixed fluorocarbon refrigerant; and

a heat exchanger configured to cool the natural gas via indirect heat exchange with the cooled mixed fluorocarbon refrigerant.

13. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, or 10-12, wherein the hydrocarbon processing system is configured to chill the natural gas for hydrocarbon dew point control.

14. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, or 10-13, wherein the hydrocarbon processing system is configured to chill the natural gas for natural gas liquid extraction.

15. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, or 10-14, wherein the hydrocarbon processing system is configured to separate methane and lighter gases from carbon dioxide and heavier gases.

16. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, or 10-15, wherein the hydrocarbon processing system is configured to prepare hydrocarbons for liquefied petroleum gas production storage.

17. The hydrocarbon processing system of any of paragraphs 1-3, 5-8, or 10-16, wherein the hydrocarbon processing system is configured to condense a reflux stream.

18. A method for liquefied natural gas (LNG) production, including:

cooling a natural gas to produce LNG in a fluorocarbon refrigeration system using a mixed fluorocarbon refrigerant; and

removing nitrogen from the LNG in a nitrogen rejection unit (NRU).

19. The method of any of paragraphs 18, including further cooling the natural gas to produce the LNG in a nitrogen refrigeration system using a nitrogen refrigerant.

20. The method of any of paragraphs 18 or 19, including further cooling the natural gas to produce the LNG in an autorefrigeration system.

21. The method of paragraph 20, including cooling at least a portion of the natural gas using a nitrogen stream separated from the natural gas via the NRU.

22. The method of any of paragraphs 18-20, wherein cooling the natural gas in the fluorocarbon refrigeration system includes:

compressing the mixed fluorocarbon refrigerant to provide a compressed mixed fluorocarbon refrigerant;

cooling the compressed mixed fluorocarbon refrigerant by indirect heat exchange with a cooling fluid to provide a cooled mixed fluorocarbon refrigerant;

passing the cooled mixed fluorocarbon refrigerant to a heat exchange area; and

heat exchanging the natural gas with the cooled mixed fluorocarbon refrigerant in the heat exchange area.

23. A hydrocarbon processing system for formation of a liquefied natural gas (LNG), including:

a mixed refrigerant cycle configured to cool a natural gas using a mixed fluorocarbon refrigerant, wherein the mixed refrigerant cycle includes a heat exchanger configured to allow for cooling of the natural gas via an indirect exchange of heat between the natural gas and the mixed fluorocarbon refrigerant;

a nitrogen rejection unit (NRU) configured to remove nitrogen from the natural gas; and

a methane autorefrigeration system configured to cool the natural gas to produce the LNG.

24. The hydrocarbon processing system of paragraph 23, wherein the mixed fluorocarbon refrigerant includes a mixture of two or more hydrofluorocarbon refrigerants.

25. The hydrocarbon processing system of any of paragraphs 2 or 24, wherein a nitrogen stream separated from the natural gas via the NRU is used to cool at least a portion of the natural gas.

26. The hydrocarbon processing system of any of paragraphs 23-25, wherein the methane autorefrigeration system includes a number of expansion devices and a number of flash drums.

[0156] While the present techniques may be susceptible to various modifications and alternative forms, the embodiments discussed herein 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 of the appended claims.

Claims

1. A hydrocarbon processing system for liquefied natural gas (LNG) production, comprising:

a fluorocarbon refrigeration system configured to cool a natural gas to produce LNG using a mixed fluorocarbon refrigerant;
a nitrogen rejection unit (NRU) configured to remove nitrogen from the LNG; and
an autorefrigeration system configured to further cool the natural gas to produce the LNG.

2. The hydrocarbon processing system of claim 1, wherein the autorefrigeration system comprises a plurality of flash drums and a plurality of expansion devices.

3. The hydrocarbon processing system of claim 1, further comprising a nitrogen refrigeration system configured to further cool the natural gas to produce the LNG using a nitrogen refrigerant.

4. The hydrocarbon processing system of claim 1, wherein at least a portion of the natural gas is cooled using a nitrogen stream separated from the natural gas via the NRU.

5. The hydrocarbon processing system of any one of claims 1 or 3-4, wherein the fluorocarbon refrigeration system comprises a single mixed refrigerant cycle or a pre-cooled mixed refrigerant cycle.

6. The hydrocarbon processing system of any one of claims 1 or 3-5, wherein the fluorocarbon refrigeration system comprises a dual mixed refrigerant cycle comprising:

a first mixed refrigerant cycle that uses a warm mixed fluorocarbon refrigerant; and
a second mixed refrigerant cycle that uses a cold mixed fluorocarbon refrigerant, wherein the first mixed refrigerant cycle and the second mixed refrigerant cycle are connected in series.

7. The hydrocarbon processing system of any one of claims 1 or 3-5, wherein the fluorocarbon refrigeration system comprises a heat exchanger configured to allow for cooling of the natural gas via an indirect exchange of heat between the natural gas and the mixed fluorocarbon refrigerant.

8. The hydrocarbon processing system of any one of claims 1, 3-5, or 7, wherein the fluorocarbon refrigeration system comprises:

a compressor configured to compress the mixed fluorocarbon refrigerant to provide a compressed mixed fluorocarbon refrigerant;
a chiller configured to cool the compressed mixed fluorocarbon refrigerant to provide a cooled mixed fluorocarbon refrigerant; and
a heat exchanger configured to cool the natural gas via indirect heat exchange with the cooled mixed fluorocarbon refrigerant.

9. The hydrocarbon processing system of any one of claims 1, 3-5, or 7-8, wherein the hydrocarbon processing system

is configured to chill the natural gas for hydrocarbon dew point control, preferably the hydrocarbon processing system is configured to chill the natural gas for natural gas liquid extraction.

5 10. The hydrocarbon processing system of any one of claims 1, 3-5, or 7-9, wherein the hydrocarbon processing system is configured to separate methane and lighter gases from carbon dioxide and heavier gases.

11. The hydrocarbon processing system of any one of claims 1, 3-5, or 7-10, wherein the hydrocarbon processing system is configured to condense a reflux stream.

10 12. A method for liquefied natural gas (LNG) production, comprising:

cooling a natural gas to produce LNG in a fluorocarbon refrigeration system using a mixed fluorocarbon refrigerant;

removing nitrogen from the LNG in a nitrogen rejection unit (NRU); and

15 further cooling the natural gas to produce the LNG in an autorefrigeration system.

13. The method of claim 12, including further cooling the natural gas to produce the LNG in a nitrogen refrigeration system using a nitrogen refrigerant.

20 14. The method of claim 12 or 13, comprising cooling at least a portion of the natural gas using a nitrogen stream separated from the natural gas via the NRU.

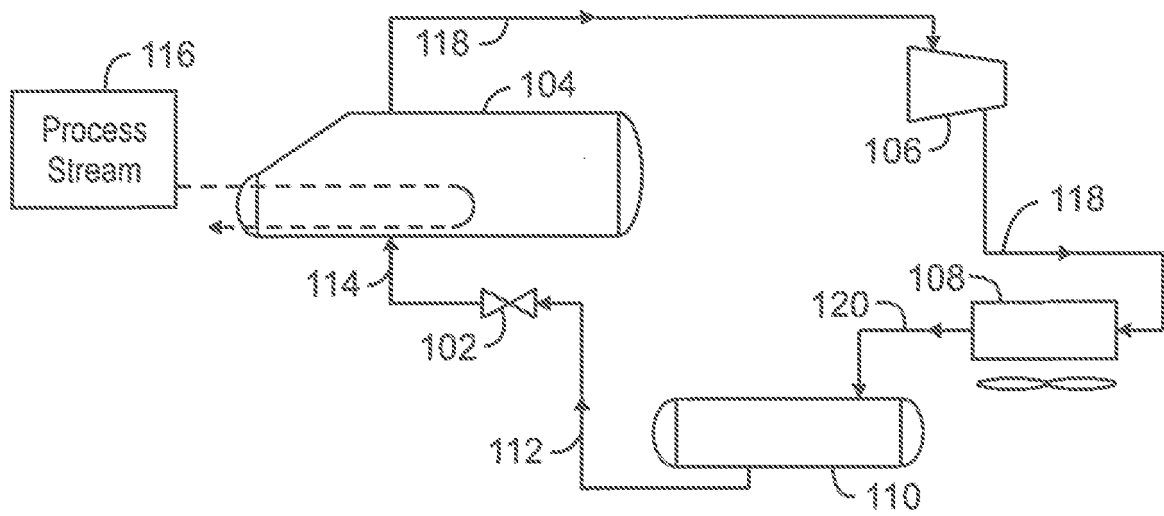
15. The method of any one of claims 12-14, wherein cooling the natural gas in the fluorocarbon refrigeration system comprises:

25 compressing the mixed fluorocarbon refrigerant to provide a compressed mixed fluorocarbon refrigerant;

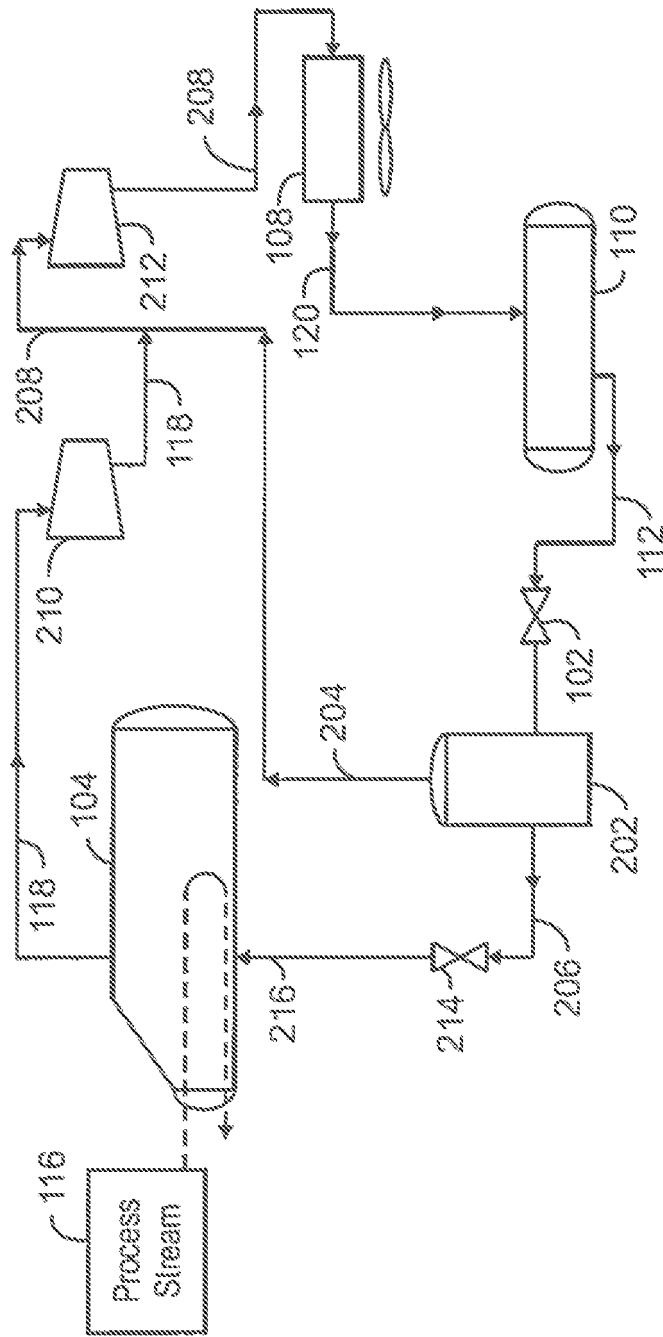
cooling the compressed mixed fluorocarbon refrigerant by indirect heat exchange with a cooling fluid to provide a cooled mixed fluorocarbon refrigerant;

passing the cooled mixed fluorocarbon refrigerant to a heat exchange area; and

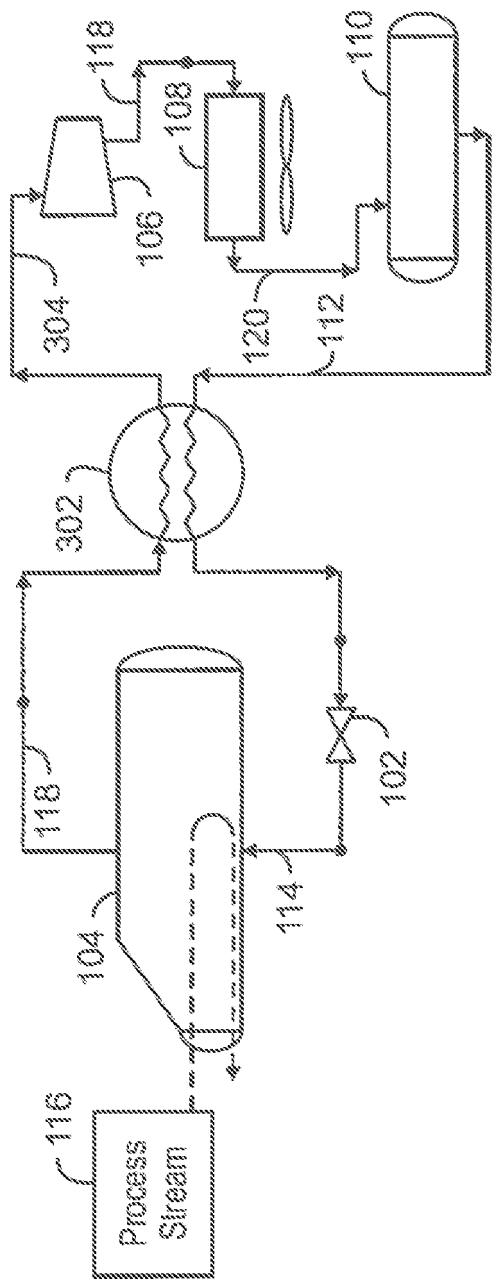
30 heat exchanging the natural gas with the cooled mixed fluorocarbon refrigerant in the heat exchange area.



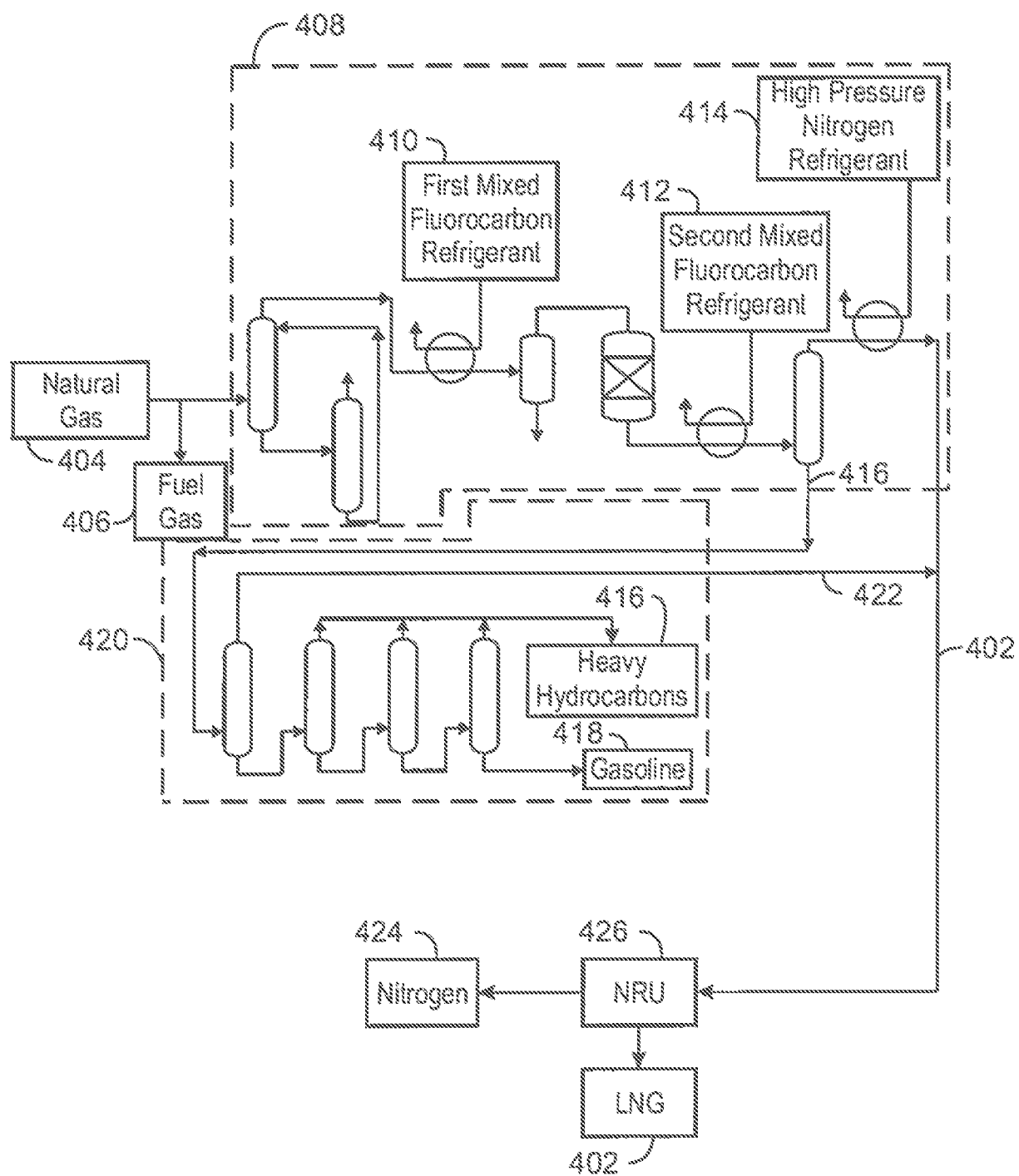
100
FIG. 1



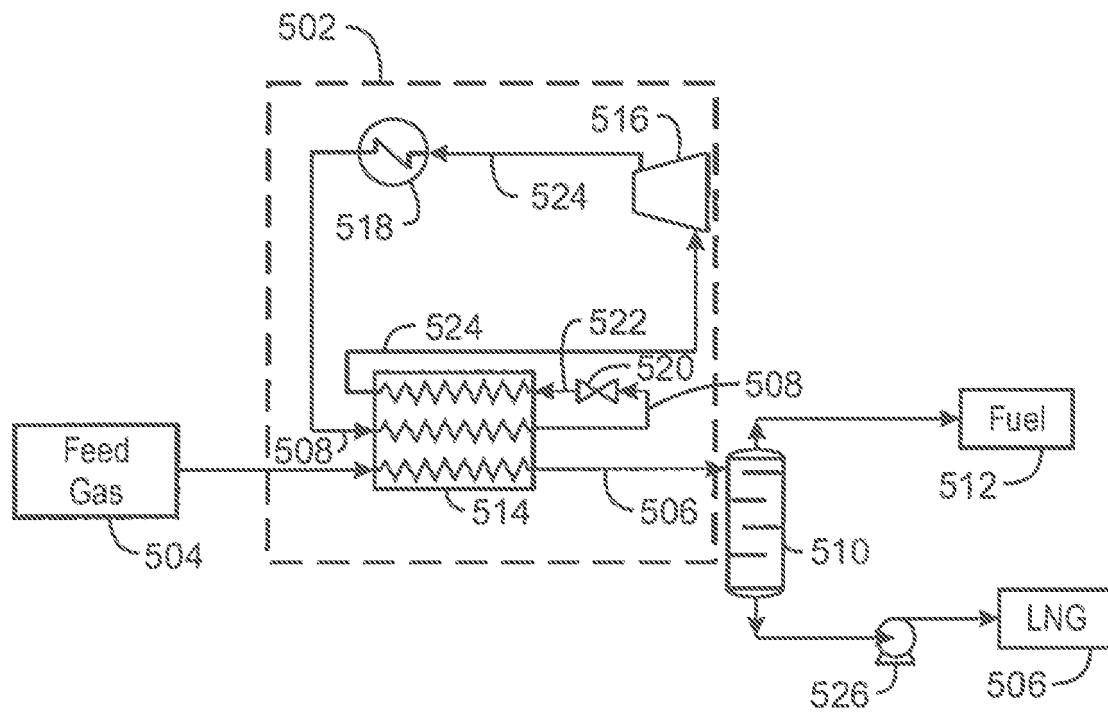
200
FIG. 2



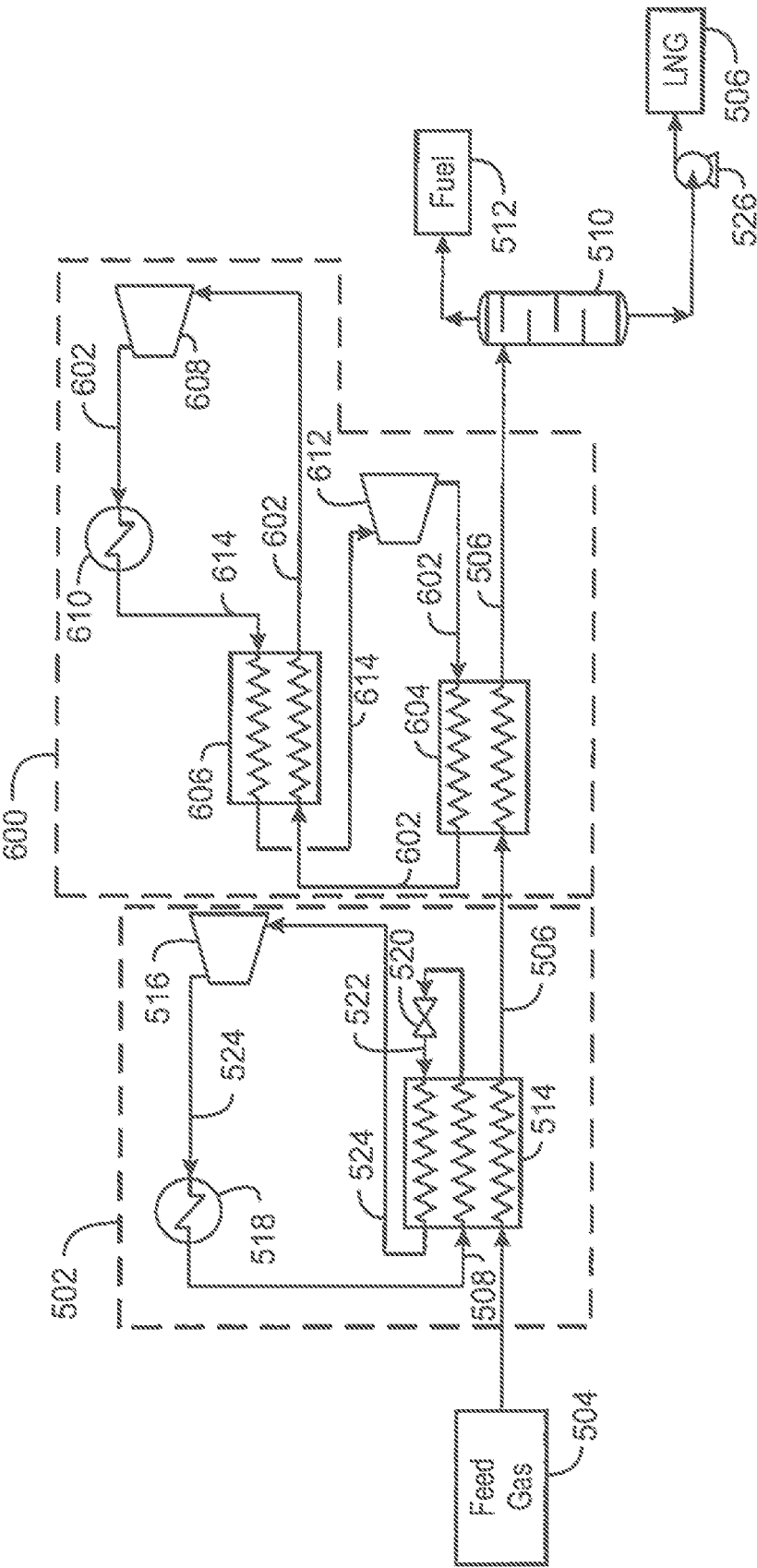
300
FIG. 3



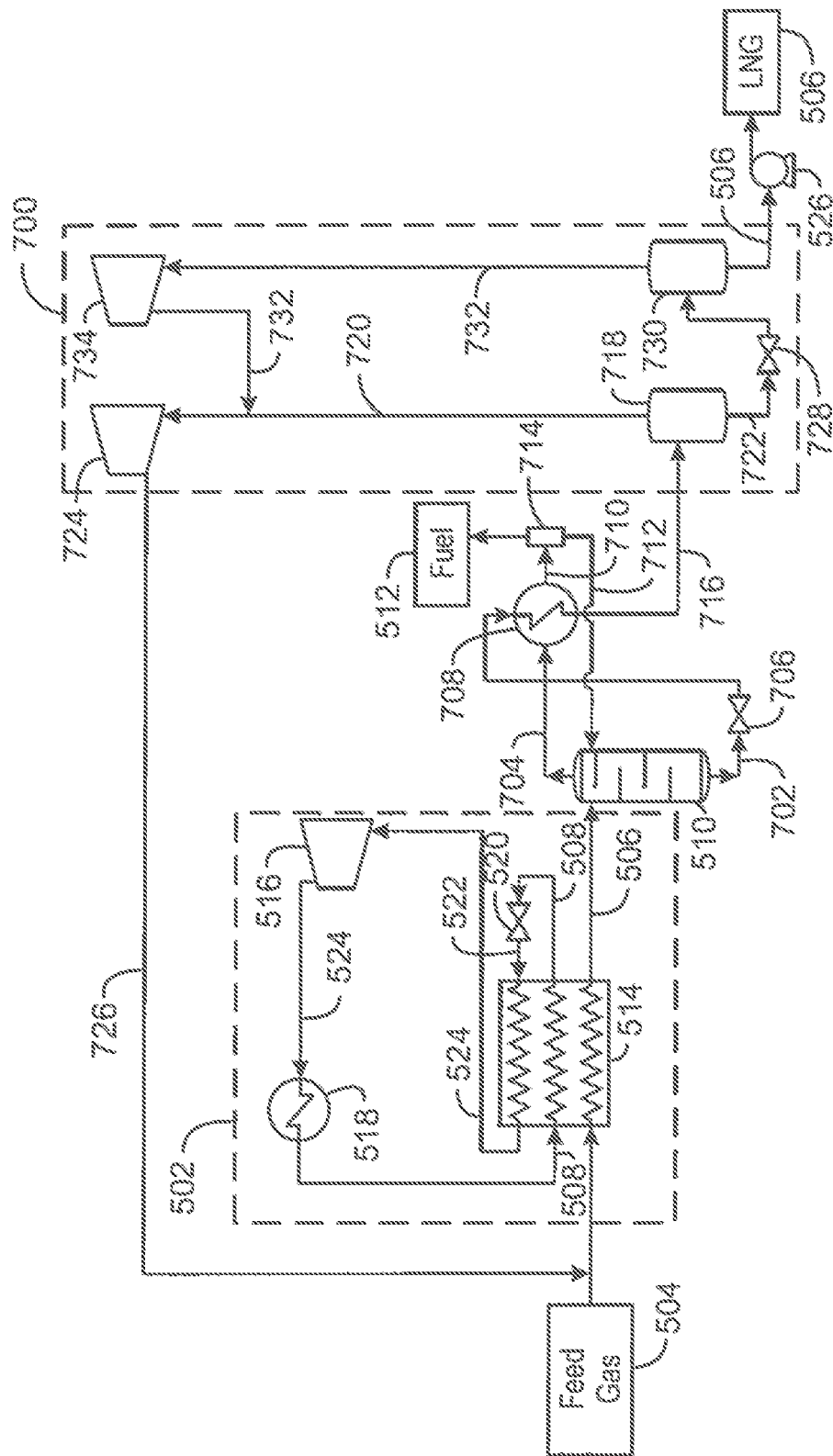
400
FIG. 4



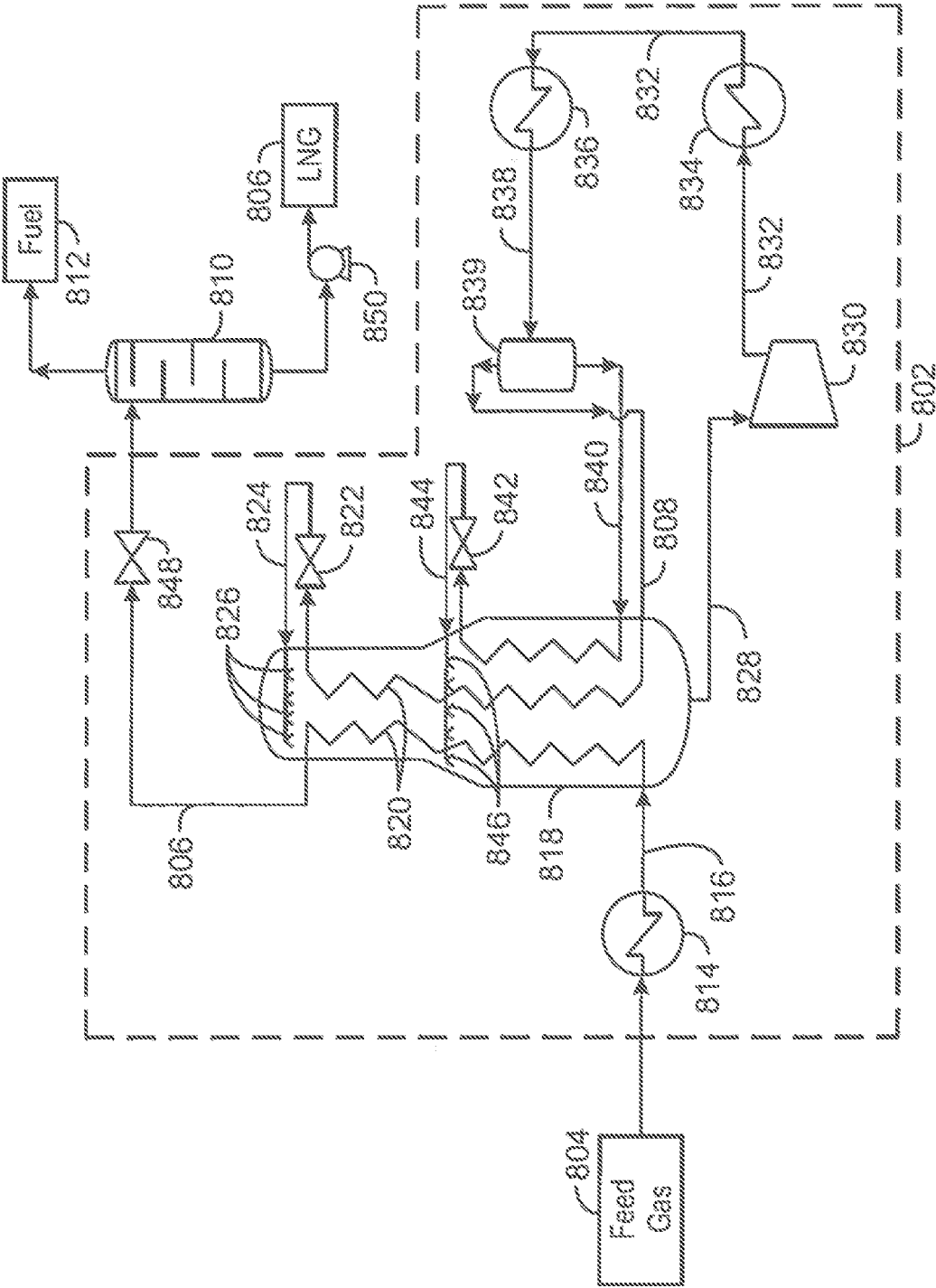
500
FIG. 5



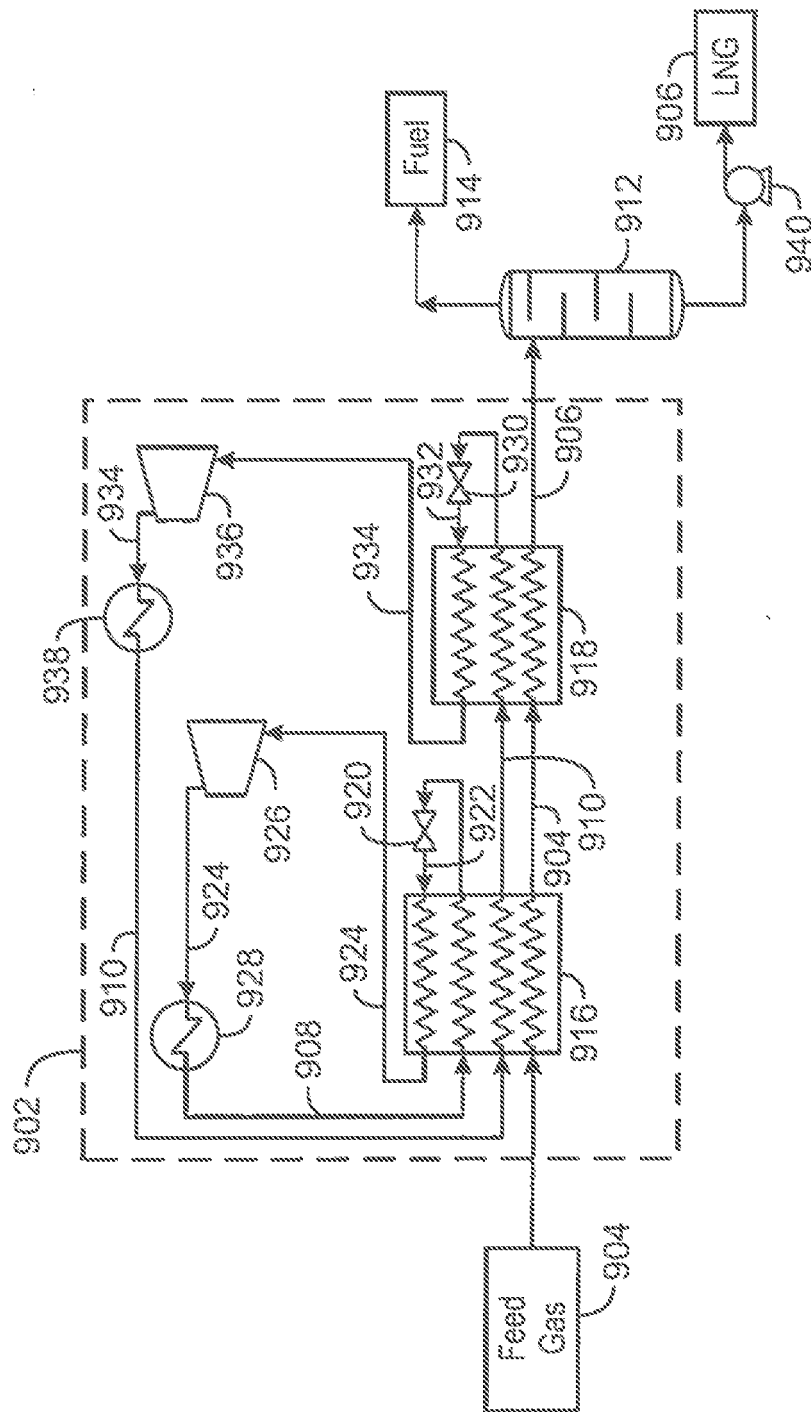
500
FIG. 6



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FIG. 7



800
FIG. 8



900
FIG. 9

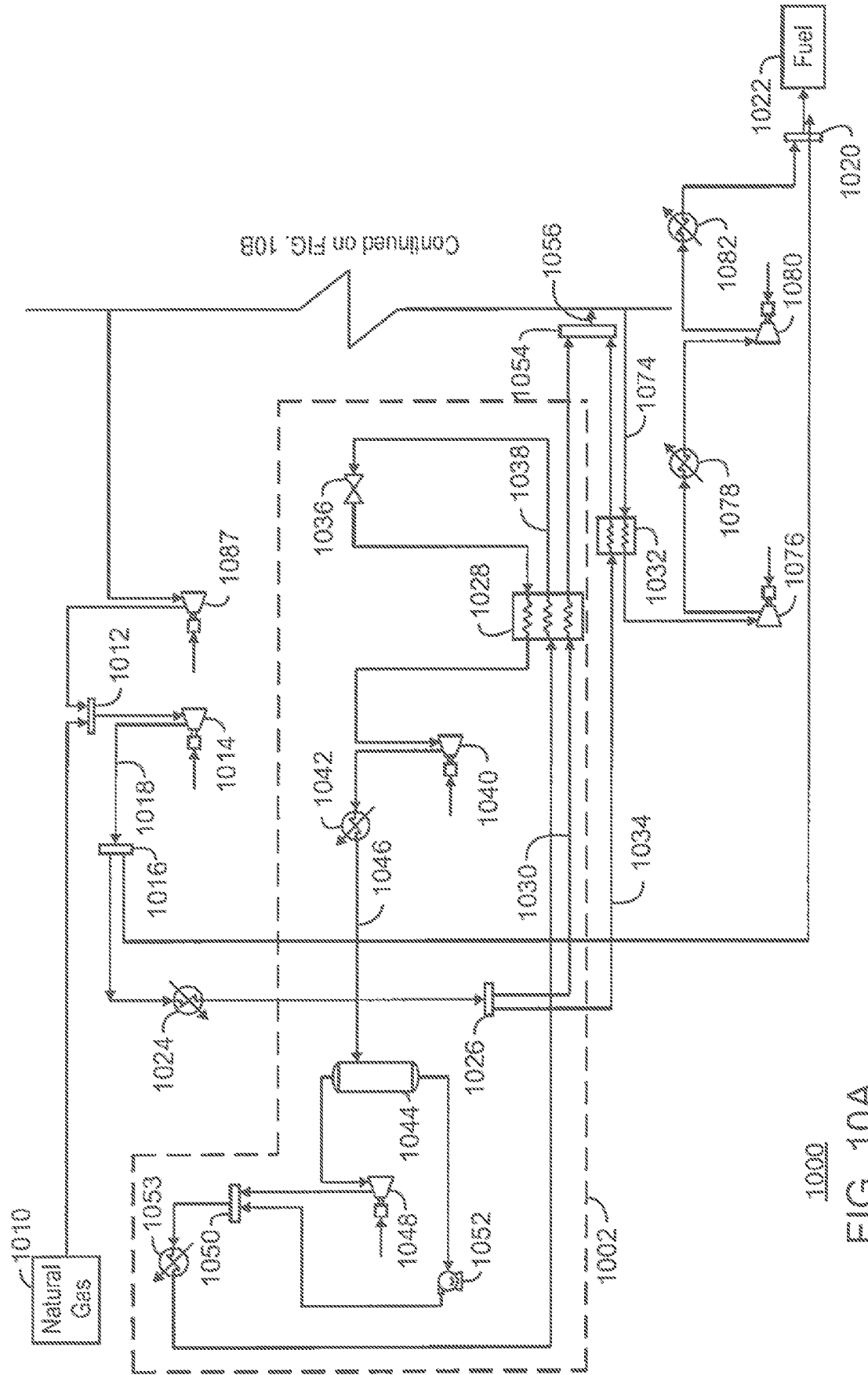


FIG. 10A

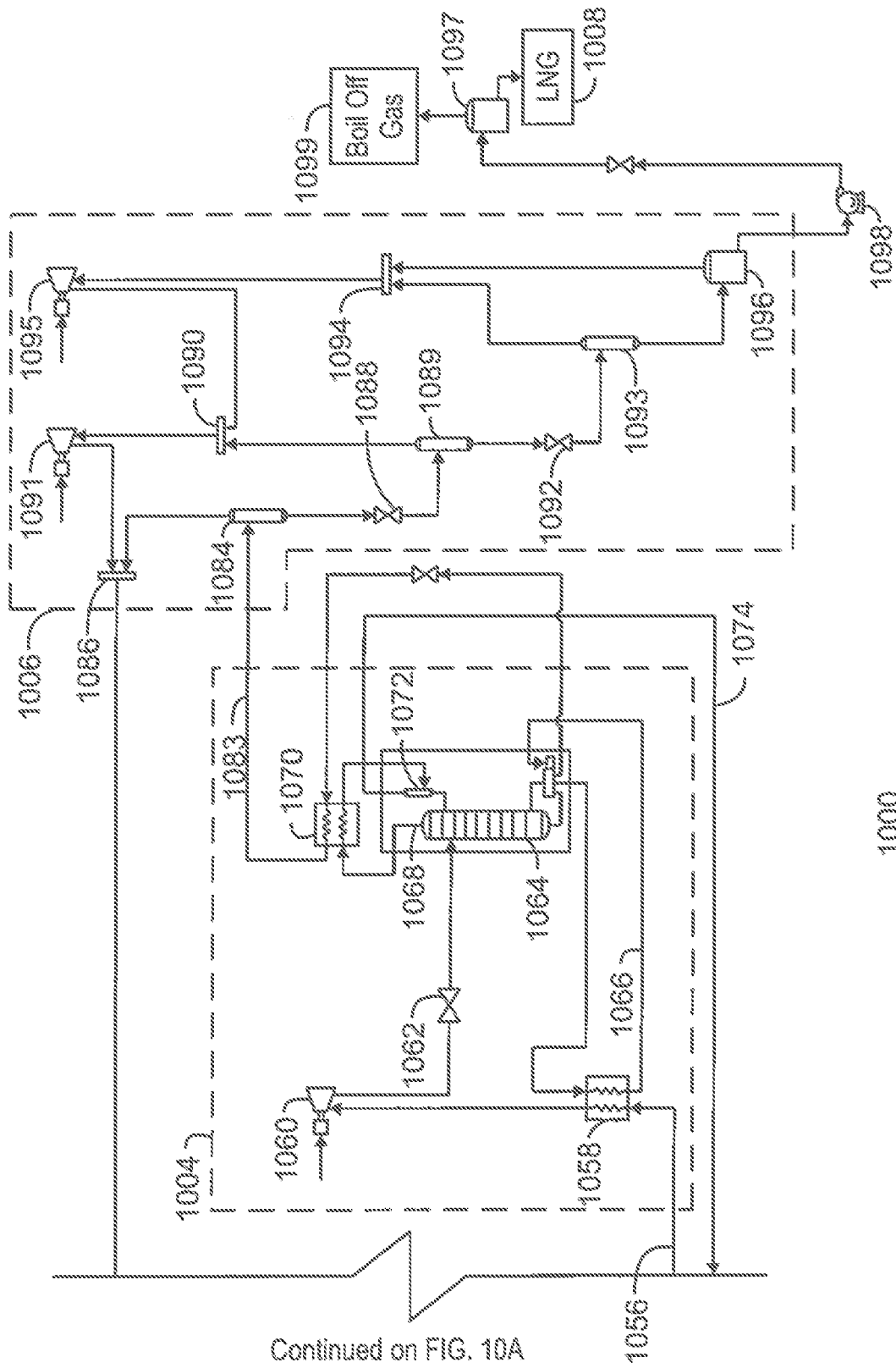
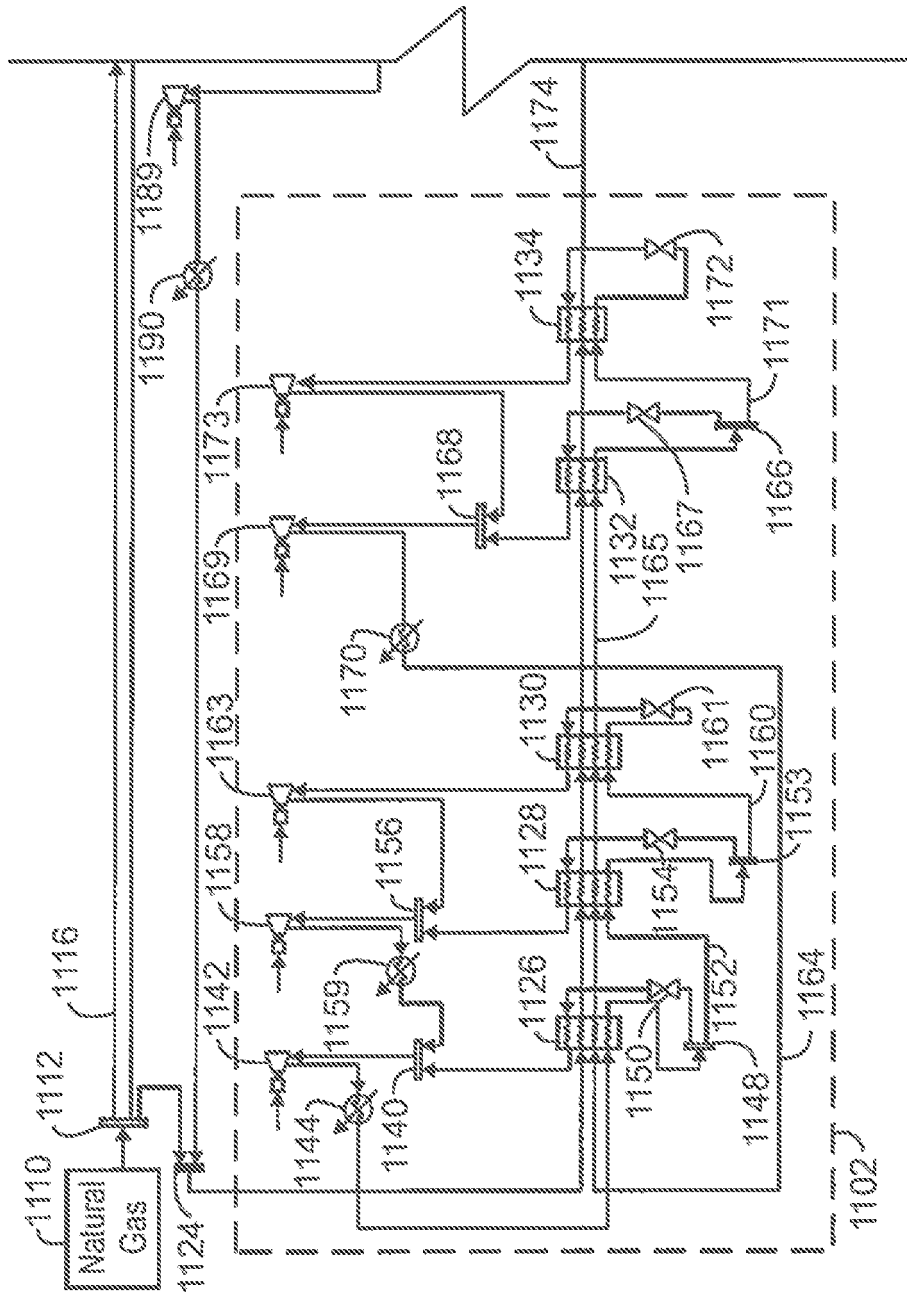


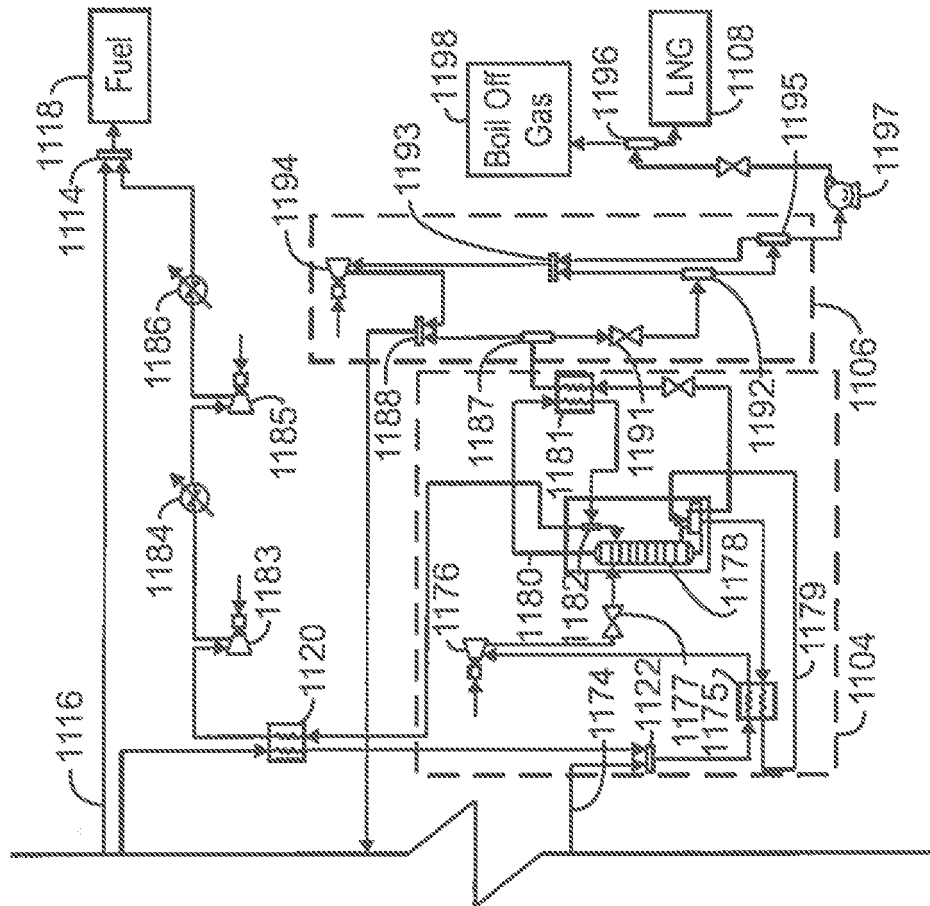
FIG. 10B

Continued on FIG. 10A

Continued on FIG. 11B

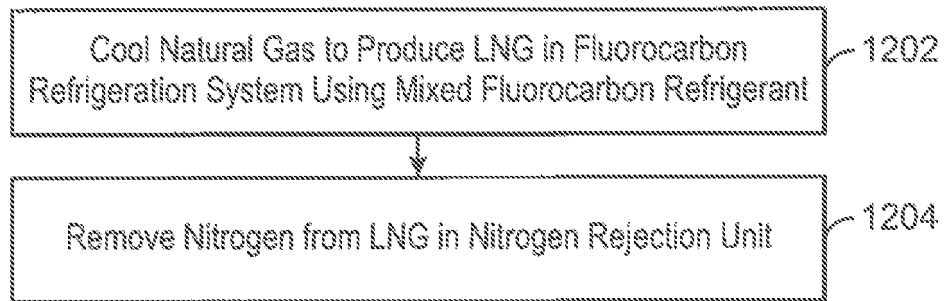


1100
FIG. 11A



Continued on FIG. 11A

1100
FIG. 11B



1200
FIG. 12



EUROPEAN SEARCH REPORT

Application Number
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Place of search Munich		Date of completion of the search 26 October 2018	Examiner Schopfer, Georg
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