

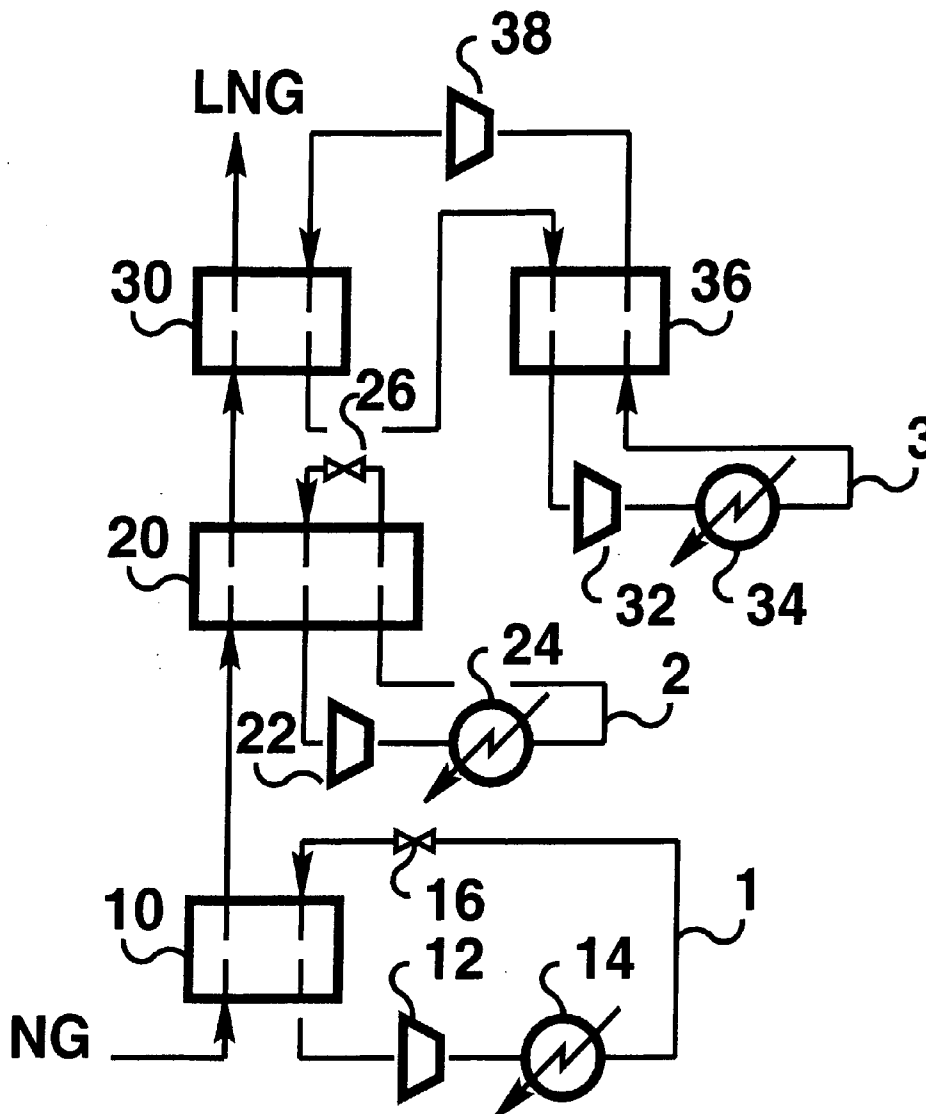


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(19) **United States**(12) **Patent Application Publication**
Roberts et al.(10) **Pub. No.: US 2008/0141711 A1**(43) **Pub. Date: Jun. 19, 2008**(54) **HYBRID CYCLE LIQUEFACTION OF
NATURAL GAS WITH PROPANE
PRE-COOLING**(22) Filed: **Dec. 18, 2006****Publication Classification**(76) Inventors: **Mark Julian Roberts**, Kempton,
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(US)(51) **Int. Cl.**
F25J 1/00 (2006.01)(52) **U.S. Cl.** **62/611**(57) **ABSTRACT**

Natural gas is liquefied in a hybrid liquefaction cycle in which the gas feed is pre-cooled using vaporizing liquefied refrigerant gas; liquefied using vaporizing mixed refrigerant comprising ethylene and at least one other refrigerant selected from hydrocarbons and halocarbons; and subcooled using a work expanded pressurized gaseous refrigerant stream. Preferably, the liquefied refrigerant gas used for precooling is propane, the mixed refrigerant does not contain ethane or nitrogen and the pressurized gaseous refrigerant is nitrogen.

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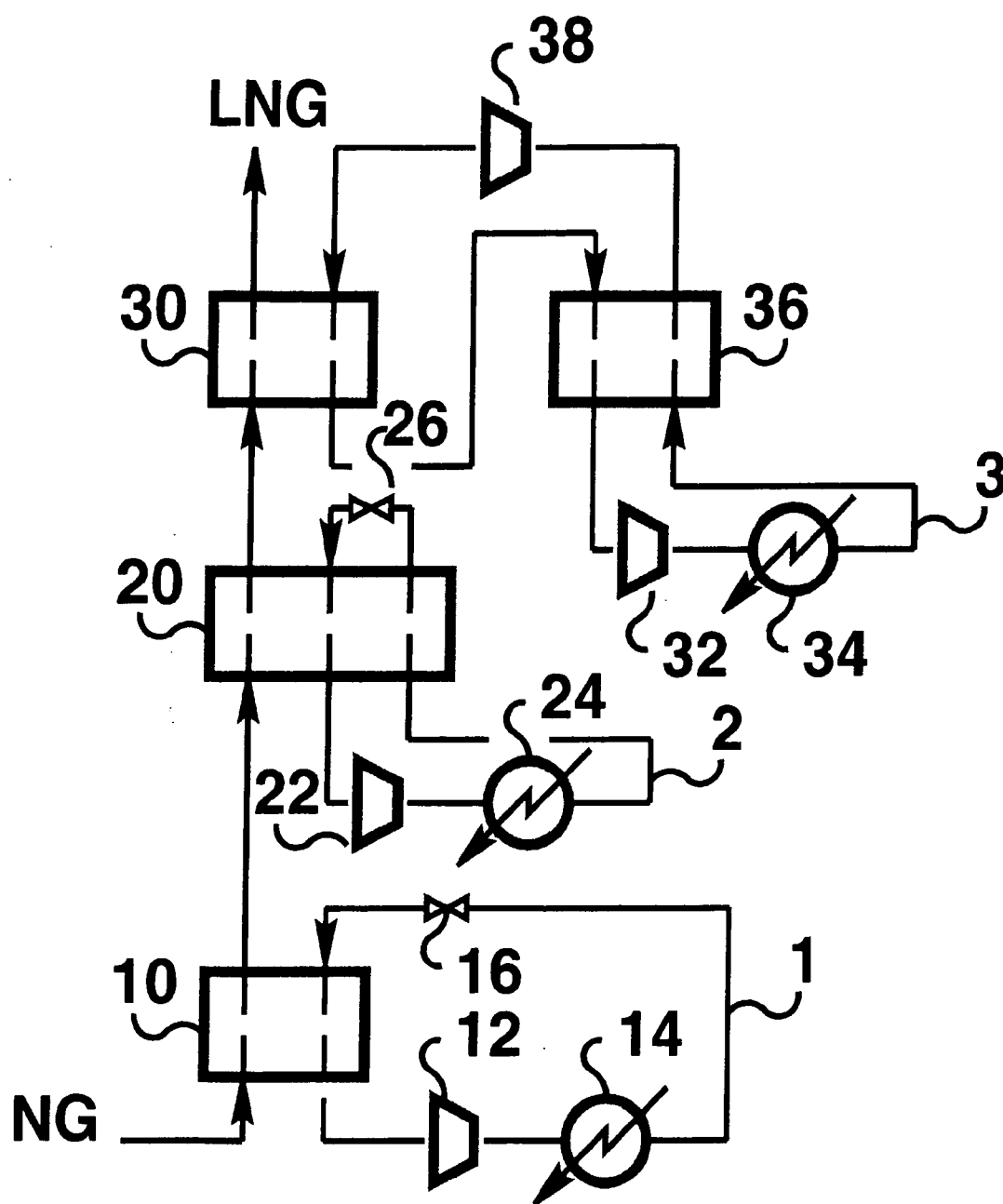


FIG. 1

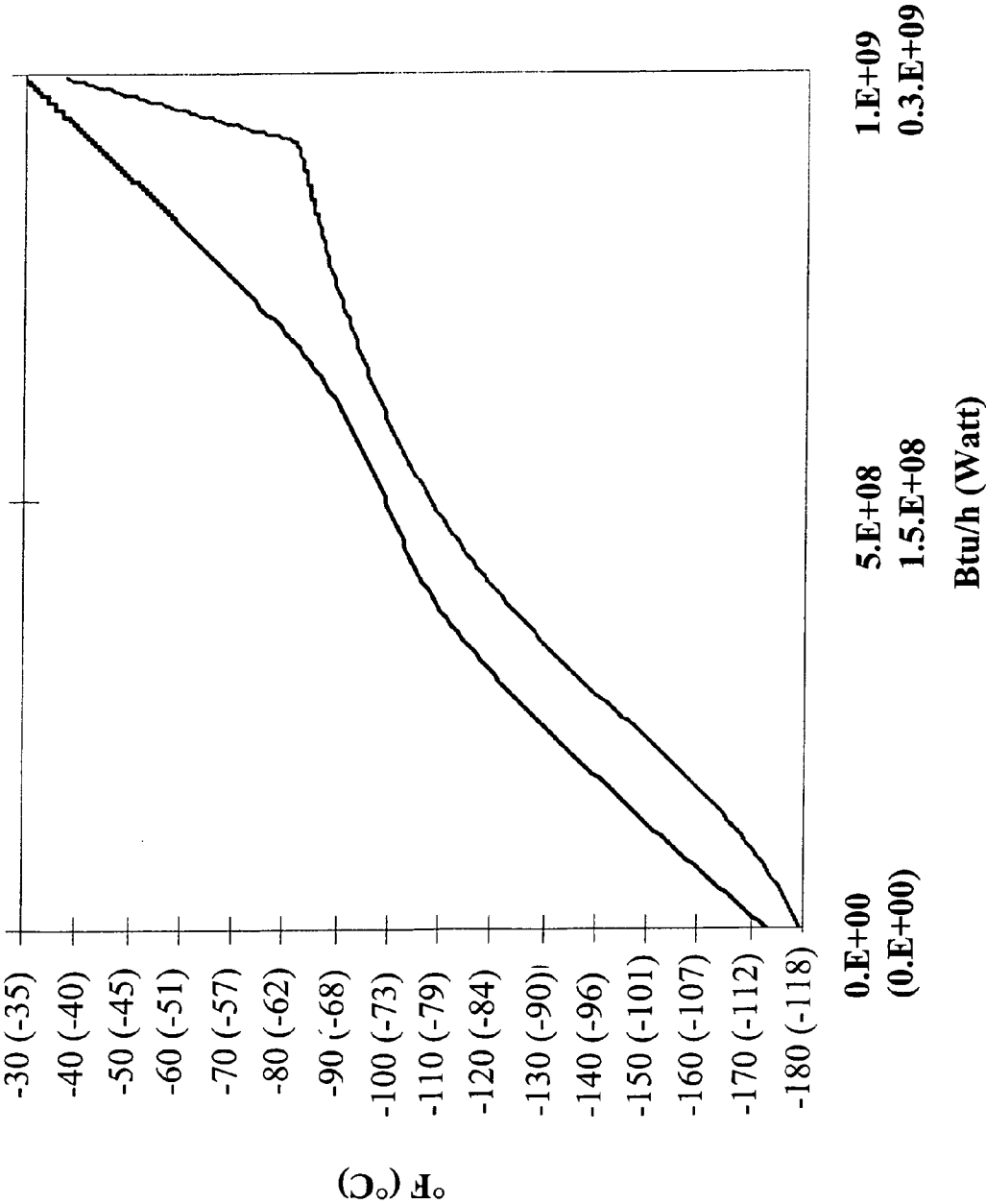


FIG. 2

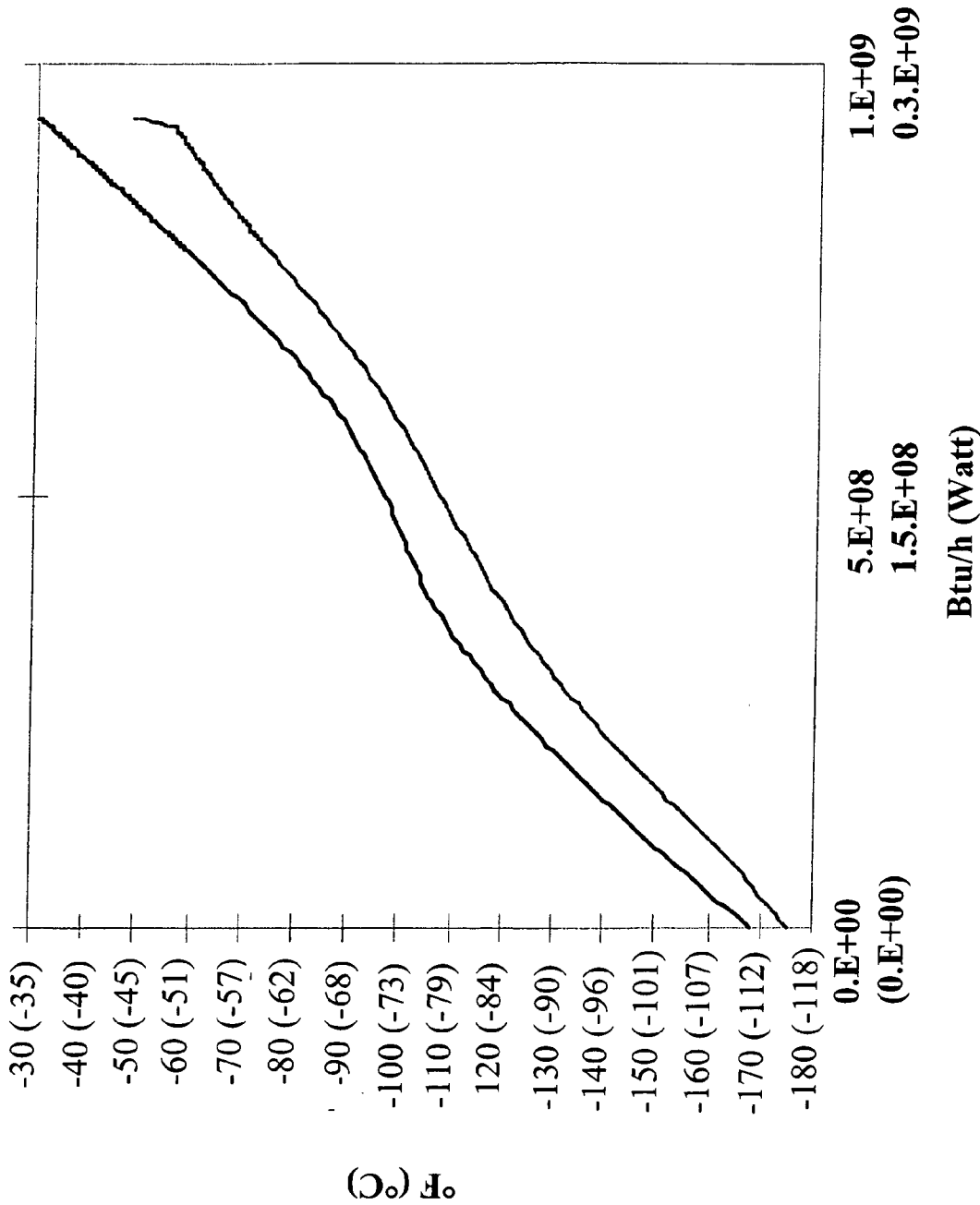


FIG. 3

HYBRID CYCLE LIQUEFACTION OF NATURAL GAS WITH PROPANE PRE-COOLING

BACKGROUND OF THE INVENTION

[0001] The present invention relates to the liquefaction of natural gas (LNG) using a hybrid cycle in which the gas is liquefied using refrigeration provided by vaporizing a refrigerant stream and the liquefied gas subcooled using refrigeration provided by work expanding a pressurized gaseous refrigerant stream. In particular, the invention provides an improved method of liquefying natural gas when the gas feed is precooled using refrigeration provided by vaporizing propane.

[0002] The production of liquefied natural gas (LNG) usually is achieved by cooling and condensing a feed gas stream against multiple refrigerant streams provided by recirculating refrigeration systems. Cooling of the natural gas feed is accomplished by various cooling process cycles such as the well-known cascade cycle in which refrigeration is provided by three different refrigerant loops. One such cascade cycle uses methane, ethane or ethylene, and propane cycles in sequence to produce refrigeration at three different temperature levels. Another well-known refrigeration cycle uses a propane pre-cooled, mixed refrigerant cycle ("C3MR") in which a mixed refrigerant mixture generates refrigeration over a selected temperature range. The mixed refrigerant can contain at least two refrigerants selected from C₁-C₅ hydrocarbons, such as for example methane, ethane, ethylene, propane and propylene, and halocarbons, such as for example chlorinated and/or fluorinated methane and ethane, and also may contain nitrogen.

[0003] The use of ethylene as a component of a mixed refrigerant for liquefying natural gas is disclosed in, for example, U.S. Pat. No. 3,645,106 (published Feb. 29, 1972), GB-A-1314174 (published Apr. 18, 1973), U.S. Pat. No. 4,229,195 (published Oct. 21, 1980), U.S. Pat. No. 4,548,629 (published Oct. 22, 1985), U.S. Pat. No. 6,062,041 (published May 16, 2000), U.S. Pat. No. 6,253,574 (published Jul. 3, 2001), U.S. Pat. No. 6,742,357 (published Jun. 1, 2004), and U.S. Pat. No. 7,086,251 (published Aug. 8, 2006). It is stated in U.S. Pat. No. 4,548,629 that, from the sole standpoint of thermodynamic efficiency, ethane is preferred over ethylene.

[0004] Another type of refrigeration process for natural gas liquefaction involves the use of an expander cycle in which gas, usually nitrogen, is first compressed and cooled to ambient conditions with air or water cooling and then is further cooled by counter-current exchange with cold low-pressure gas. The cooled gas stream is then work expanded through a turbo-expander to produce a cold low pressure stream. The cold gas stream is used to cool the natural gas feed and the high pressure gas stream. The work produced by expansion can be used to drive a nitrogen booster compressor connected to the shaft of the expander. In this process, the cold expanded gas is used to liquefy the natural gas and also to cool the compressed gas in the same heat exchanger. The cooled pressurized gas is further cooled in the work expansion step to provide the cold refrigerant.

[0005] In hybrid cycles for liquefaction of natural gas, the natural gas feed is liquefied using refrigeration provided by vaporizing a mixed refrigerant stream and the liquefied gas subcooled using refrigeration provided by work expanding a pressurized gaseous refrigerant stream. Such hybrid processes are described in DE-A-2440215 (published Mar. 4, 1976) and U.S. Pat. No. 6,308,531 (published Oct. 30, 2001 and the entire contents of which are incorporated herein by way of this reference). Recently, such processes have been

commercialized under the Trade Mark AP-X by Air Products & Chemical Inc. In the AP-X® process, the natural gas feed can be precooled by a propane cycle and the mixed refrigerant comprises methane, ethane and propane.

[0006] In the process of DE-A-2440215 the natural gas feed is precooled by vaporization of the mixed refrigerant stream but in the some of the exemplified embodiments of U.S. Pat. No. 6,308,531, the feed is precooled by vaporizing propane. Neither DE-A-2440215 nor U.S. Pat. No. 6,308,531 discloses the use of ethylene in the mixed refrigerant of a hybrid process.

[0007] There is a need to optimize the mixed composition in the second refrigerant circuit for the liquefaction step of the three-circuit hybrid liquefaction cycle which uses propane refrigeration for precooling, mixed refrigeration for liquefaction, and expansion of gaseous nitrogen for subcooling. In particular, it is an object of the present invention to reduce power consumption, increase production, and/or provide for more even power distribution between the three circuits allowing better selection of drivers such as gas turbines. The solution should be applicable to new LNG plants and for retrofitting and debottlenecking existing LNG plants.

BRIEF SUMMARY OF THE INVENTION

[0008] It has been found that the aforementioned three-circuit hybrid liquefaction cycle is improved if the mixed refrigerant comprises ethylene and at least one other refrigerant selected from hydrocarbons and halocarbons but, preferably, does not contain ethane.

[0009] In its broadest aspect, the present invention provides a method of liquefying natural gas which comprises:

[0010] precooling a natural gas feed stream to a temperature below ambient temperature with refrigeration provided by vaporizing a liquefied refrigerant gas;

[0011] liquefying the precooled gas stream with refrigeration provided by vaporizing a mixed refrigerant comprising two or more refrigerants selected from hydrocarbons and halocarbons; and

[0012] subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous refrigerant stream,

characterized in that the mixed refrigerant comprises ethylene.

[0013] In accordance with a preferred embodiment, the method comprises:

[0014] precooling the natural gas feed stream to a temperature not below about -40° F. (-40° C.) with refrigeration provided by vaporizing a single component liquefied refrigerant gas;

[0015] liquefying the precooled gas stream with refrigeration provided by vaporizing an essentially ethane-free mixed refrigerant comprising methane, ethylene and propane; and

[0016] subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous nitrogen stream.

[0017] In accordance with the most preferred embodiment, the method comprises:

[0018] precooling a natural gas feed stream to a temperature of about -30° F. (-35° C.) with refrigeration provided by vaporizing propane;

[0019] liquefying the precooled gas stream with refrigeration provided by vaporizing a mixed refrigerant consisting of methane, ethylene and propane; and

[0020] subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous nitrogen stream.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0021] FIG. 1 is a simplified, schematic diagram of a three-circuit hybrid process for liquefying natural gas.

[0022] FIG. 2 is a graph showing the temperature profile of the liquefier heat exchanger that uses a methane-ethane-propane mixture as a refrigerant in the second refrigerant circuit of the three-circuit hybrid of FIG. 1.

[0023] FIG. 3 is a graph showing the temperature profile of the liquefier heat exchanger that uses a methane-ethylene-propane mixture as a refrigerant in the second refrigerant circuit of the three-circuit hybrid of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present invention relates to the liquefaction of natural gas (LNG) using a three-circuit hybrid cycle in which the gas is precooled below ambient temperature using refrigeration provided by vaporizing a liquefied refrigerant gas, preferably propane; the precooled gas is liquefied using refrigeration provided by vaporizing a mixed refrigerant stream and the liquefied gas is subcooled using refrigeration provided by work expanding a pressurized gaseous refrigerant stream. The invention resides in the composition of the mixed refrigerant.

[0025] According to the invention, there is provided a method of liquefying natural gas which comprises:

[0026] precooling a natural gas feed stream to a temperature below ambient temperature with refrigeration provided by vaporizing a liquefied refrigerant gas;

[0027] liquefying the precooled gas stream with refrigeration provided by vaporizing a mixed refrigerant comprising ethylene and one or more refrigerants selected from hydrocarbons and halocarbons; and

[0028] subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous refrigerant stream.

[0029] Usually, the natural gas feed stream will be pre-cooled to a temperature not below about -40°F. (-40°C.), preferably to a temperature not below about -35°F. (-37°C.) and especially to a temperature of about -30°F. (-35°C.). The liquefied refrigerant gas can be any of those known for use in pre-cooling natural gas to such temperatures but preferably consists of a single component such as propylene, ethane, a halocarbon or, preferably, propane.

[0030] The mixed refrigerant comprises ethylene and one or more refrigerants selected from hydrocarbons and halocarbons. Suitable hydrocarbon refrigerants for use in the invention include methane, propane, i-butane, butane, and i-pentane. Representative halocarbon refrigerants include R22 (chlorodifluoromethane), R23 (trifluoromethane), R32 (difluoromethane), R134a (tetrafluoroethane), and R410a (mixed difluoromethane and pentafluoroethane). The mixed refrigerant can include nitrogen but, except when the present invention is applied to an existing liquefaction plant employing a nitrogen-containing mixed refrigerant, it is preferred that it consists only of hydrocarbons and optionally halocarbons. Preferably, the mixed refrigerant will consist of ethylene and one or more other refrigerants selected from C_1 to C_5 hydrocarbons. It is highly preferred that the mixed refrigerant does not comprise ethane and suitably the mixed refrigerant comprises or consists of methane, ethylene and propane.

[0031] It is highly preferred that the pressurized gaseous refrigerant stream is nitrogen although other gases such as argon could be used.

[0032] In a preferred embodiment, the method of liquefying natural gas comprises:

[0033] precooling the natural gas feed stream to a temperature not below about -40°F. (-40°C.) with refrigeration provided by vaporizing a single component liquefied refrigerant gas;

[0034] liquefying the precooled gas stream with refrigeration provided by vaporizing an essentially ethane-free mixed refrigerant comprising methane, ethylene and propane; and

[0035] subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous nitrogen stream.

[0036] It is particularly preferred that the method of liquefying natural gas comprises:

[0037] precooling a natural gas feed stream to a temperature of about -30°F. (-35°C.) with refrigeration provided by vaporizing propane;

[0038] liquefying the precooled gas stream with refrigeration provided by vaporizing a mixed refrigerant consisting of methane, ethylene and propane; and

[0039] subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous nitrogen stream.

[0040] Referring to the embodiment illustrated by the simplified, schematic diagram on FIG. 1, natural gas (NG) is pre-cooled in heat exchanger(s) 10, liquefied in liquefier heat exchanger 20, and subcooled in subcooler heat exchanger 30. The natural gas liquefaction process comprises three refrigerant circuits. The first circuit (1) provides precooling. Propane is compressed in compressor 12, cooled and condensed by air or cooling water in heat exchanger(s) 14, expanded through valve(s) 16 to different pressure levels, and evaporated in multi-stream heat exchanger or a series of kettles shown as heat exchanger(s) 10. Typically, the propane pre-cools both the natural gas feed and refrigerants in the second and third circuits (which refrigerant precooling is not shown for simplicity) to about -30°F. (-35°C.).

[0041] Although in known three-circuit hybrid processes, the first circuit usually uses a mixed refrigerant of suitable composition, the use of propane at multiple pressure levels is simpler and at least as efficient. The efficiency loss in using a mixed refrigerant is due to the fact that it is typically condensed at close-to-ambient temperature by heat exchange with air or cooling water over a range of temperatures and the condenser cooling curves are relatively far apart.

[0042] The second circuit provides refrigeration for the liquefaction. It uses a mixed refrigerant that comprises ethylene, preferably with very little or no ethane. Typical components for use in the present invention are methane, ethylene, and propane. The mixed refrigerant is compressed in compressor 24, pre-cooled by air or water and liquefied by heat exchange with refrigerant in the first circuit in heat exchanger(s) 24, further cooled in the liquefier heat exchanger 20, expanded through valve 26 or a hydraulic turbine, and evaporated in the same liquefier heat exchanger 20 to provide refrigeration for the condensing natural gas stream.

[0043] Typically the mixed refrigerant in three-circuit hybrid processes evaporates at a pressure of 64 psia (0.44 MPa). At this pressure, the boiling points of methane, ethylene, ethane, and propane are about -220°F. (-140°C.), -100°F. (-73.3°C.), -68°F. (-55.5°C.), and 29°F. (-1.7°C.), respectively. In

accordance with an embodiment of the present invention, the mixed refrigerant consists of methane, ethylene and propane and a comparative refrigerant consists of methane, ethane and propane. For the comparative mixture, the boiling point difference between the light component (methane) and the middle component (ethane) is 152° F. (84.5° C.) and the boiling point difference between the middle component and the heavy component (propane) is 97° F. (53.8° C.). For the mixture of the invention, the boiling point difference between the light component (methane) and the middle component (ethylene) is 120° F. (66.7° C.) and the boiling point difference between the middle component and the heavy component (propane) is 129° F. (71.6° C.). Therefore, unlike the boiling point of ethane, the boiling point of ethylene is close to the middle of the boiling range thereby allowing better utilization of all three of the mixed refrigerant components.

[0044] Usually, the liquefaction step cools the natural gas to a temperature not below about -190° F. (-125° C.). Typically the liquefaction step cools the natural gas from a temperature of about -30° F. (-35° C.), which is the temperature of evaporating propane in the first circuit, to a temperature of about -170° F. (-112° C.), which is towards the middle of the methane-ethylene-propane boiling range. If the first refrigerant circuit used a mixed refrigerant instead of propane, the precooling typically would be to a significantly lower temperature of about -45° F. (-43° C.), and the benefit of using ethylene in the second circuit is lower. Further, there is no benefit in using ethylene instead of ethane in the first (mixed) refrigerant circuit.

[0045] Ethylene does not offer the same advantage over ethane in a conventional C3MR process. In such processes, the mixed refrigerant typically contains nitrogen and provides cooling to about -240° F. (-150° C.). It is partially liquefied and separated into liquid and vapor. If ethylene is used, it escapes to the vapor phase and is not as useful as ethane in balancing the warm end of the heat exchanger.

[0046] The third refrigerant circuit subcools the liquefied natural gas to a temperature usually not below about -250° F. (-155° C.). Typically the third refrigerant circuit subcools the liquefied natural gas from a temperature of about -170° F. (-112° C.) to a temperature of about -240° F. (-150° C.). This circuit uses works expansion of gaseous nitrogen (the reverse-Brayton cycle). Nitrogen is compressed in compressor 32, precooled in heat exchanger(s) 34, cooled in the economizer heat exchanger 36, expanded in turbine(s) 38 and warmed back up in the subcooler heat exchanger 30. Typically, there are two nitrogen turbines but only one is shown for simplicity. The reverse-Brayton cycle is at least as efficient as mixed refrigerant cooling in this temperature range and the equipment is simpler.

[0047] FIG. 2 shows the temperature profile of the liquefier heat exchanger (24) when using the methane-ethane-propane mixed refrigerant in the second refrigerant circuit and FIG. 3 shows the corresponding profile for the methane-ethylene-propane mixture. As can be seen, the cooling curves are closer together for the methane-ethylene-propane mixture and hence the process is thermodynamically more reversible.

EXAMPLE

[0048] A plant as shown in FIG. 1 liquefies 33,000 tonne/day of natural gas using the propane circuit to precool natural gas to about -30° F. (-35° C.), the mixed refrigerant ("MR") circuit to liquefy it and cool it to about -173° F. (-114° C.), and the nitrogen circuit to subcool it to about -239° F. (-150.5° C.).

[0049] Run 1:

[0050] The plant was operated using an optimized MR composition consisting of 45.4% methane, 53.7% ethane, and 0.9% propane on a molar basis and the results are set forth in Tables 1 and 2. The propane compressor power is 50.5 MW; the MR compressor power is 124.9 MW and the nitrogen compressor power is 99.5 MW (i.e. 20% lower than the MR compressor power). Thus, the total plant power consumption is 274.9 MW.

[0051] Run 2:

[0052] The MR composition of Run 1 was replaced by an optimized MR composition consisting of 33.0% methane, 54.6% ethylene, and 12.4% propane on molar basis and the results also are set forth in Tables 1 and 2. The presence of ethylene allows better utilization of propane at the warm end. The propane compressor power is 44.1 MW (i.e. 13% lower than in Run 1). The MR compressor power is 119.4 MW (i.e. 4.4% lower than in Run 1) and the nitrogen compressor power is 107.0 MW (i.e. 7.5% higher than in Run 1; 10% lower than the MR compressor power of Run 2). The total plant power consumption is 270.5 MW (i.e. 1.6% lower than in Run 1). Thus, the overall power consumption was reduced while the power was shifted from propane and MR compression to nitrogen compression. The lower power consumption also means that higher production is possible for equal power.

[0053] If the same gas turbines of about 116-MW are chosen for both MR and nitrogen compression, then the power saving from using ethylene instead of ethane is 2.5%.

[0054] Other embodiments and benefits of the invention will be apparent to those skilled in the art from a consideration of this specification or from practice of the invention disclosed herein. It is intended that this specification be considered as exemplary only with modifications and variations being within the scope and spirit of the invention as defined by the following claims.

TABLE 1

Stream	Run					
	2 (Invention) Feed (Mole Fraction)	1 (Comparative) Feed (Mole Fraction)	2 (Invention) LNG (Mole Fraction)	1 (Comparative) LNG (Mole Fraction)	2 (Invention) MR (Mole Fraction)	1 (Comparative) MR (Mole Fraction)
N ₂	0.020798	0.020798	0.006615	0.006615	0	0
CO ₂	0.0036	0.0036	0	0	0	0
CH ₄	0.947405	0.947405	0.966381	0.966381	0.329563	0.454214
C ₂ H ₄	0	0	0	0	0.546465	0
C ₂ H ₆	0.015898	0.015898	0.017509	0.017509	0	0.537237
C ₃ H ₈	0.005299	0.005299	0.005828	0.005828	0.123972	0.008549
i-C ₄ H ₁₀	0.0011	0.0011	0.001202	0.001202	0	0
n-C ₄ H ₁₀	0.0018	0.0018	0.001959	0.001959	0	0
i-C ₅ H ₁₂	0.0007	0.0007	0.000249	0.000249	0	0

TABLE 1-continued

Stream	Run					
	2 (Invention) Feed (Mole Fraction)	1 (Comparative) Feed (Mole Fraction)	2 (Invention) LNG (Mole Fraction)	1 (Comparative) LNG (Mole Fraction)	2 (Invention) MR (Mole Fraction)	1 (Comparative) MR (Mole Fraction)
n-C ₅ H ₁₂	0.0005	0.0005	0.000143	0.000143	0	0
C ₆ H ₁₄	0.0006	0.0006	0.000059	0.000059	0	0
C ₇ H ₁₆	0.0023	0.0023	0.000057	0.000057	0	0
Total Flow	lbmol/h	175733	175733	1159350	159349	149187
	(Kgmol/h)	79711.3	79711.3	72279.8	72279.5	67670.1
Total Flow	lb/h	3020731	3020731	2660367	2660356	3891470
	(Kg/h)	1370180.6	1370180.6	1206722.2	1206717.3	1765141.2
Temperature	° F.	51	51	-260.854	-260.854	48.2
	(° C.)	10.5	10.5	-127.141	-127.141	9.0
Pressure	psi	957.2	957.2	15.2	15.2	893.4
	(kPa)	6600	6600	104.8	104.8	6160

TABLE 2

	Invention	Comparative
Power	270.48 MW	274.92 MW
Power difference	0 MW	4.44 MW
Power difference	0.00%	1.64%
C ₃ H ₈ compressor	44.11 MW	50.51 MW
MR compressor	119.40 MW	124.89 MW
N ₂ compressor	106.97 MW	99.53 MW

1. A method of liquefying natural gas which comprises: precooling a natural gas feed stream to a temperature below ambient temperature with refrigeration provided by vaporizing a liquefied refrigerant gas; liquefying the precooled gas stream with refrigeration provided by vaporizing a mixed refrigerant comprising two or more refrigerants selected from hydrocarbons and halocarbons; subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous refrigerant stream characterized in that the mixed hydrocarbon refrigerant comprises ethylene.
2. The method of claim 1, wherein the natural gas feed stream is precooled to a temperature not below about -40° F. (-40° C.)
3. The method of claim 2, wherein the natural gas feed stream is precooled to a temperature not below about -35° F. (-37° C.)
4. The method of claim 3, wherein the natural gas feed stream is precooled to a temperature of about -30° F. (-35° C.)
5. The method of claim 1, wherein the liquefied refrigerant gas used for the pre-cooling consists of a single component.
6. The method of claim 5, wherein the single component is propane.
7. The method of claim 1, wherein the mixed refrigerant does not comprise ethane.
8. The method of claim 1, wherein the mixed refrigerant comprises ethylene and one or more refrigerants selected from hydrocarbons and halocarbons

9. The method of claim 8, wherein the mixed refrigerant consists of ethylene and one or more refrigerants selected from C₁ to C₅ hydrocarbons.

10. The method of claim 9, wherein the mixed refrigerant does not comprise ethane.

11. The method of claim 1, wherein the mixed refrigerant comprises methane, ethylene and propane.

12. The method of claim 11, wherein the mixed refrigerant consist of methane, ethylene and propane.

13. The method of claim 1, wherein the pressurized gaseous refrigerant stream is nitrogen.

14. A method of liquefying natural gas which comprises: precooling a natural gas feed stream to a temperature not below about -40° F. (-40° C.) with refrigeration provided by vaporizing a single component liquefied refrigerant gas;

liquefying the precooled gas stream with refrigeration provided by vaporizing an essentially ethane-free mixed refrigerant comprising methane, ethylene and propane; and

subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous nitrogen stream.

15. The method of claim 14, wherein the natural gas feed stream is precooled to a temperature of about -30° F. (-35° C.)

16. The method of claim 14, wherein the liquefied refrigerant gas used for the pre-cooling is propane.

17. The method of claim 14, wherein the mixed refrigerant consist of methane, ethylene and propane.

18. A method of liquefying natural gas which comprises: precooling a natural gas feed stream to a temperature of about -30° F. (-35° C.) with refrigeration provided by vaporizing propane;

liquefying the precooled gas stream with refrigeration provided by vaporizing a mixed refrigerant consisting of methane, ethylene and propane; and

subcooling the liquefied stream with refrigeration by work expanding a pressurized gaseous nitrogen stream.

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