TITLE OF THE INVENTION:

# INTEGRATED MULTIPLE-LOOP REFRIGERATION PROCESS FOR GAS LIQUEFACTION

## BACKGROUND OF THE INVENTION

**[0001]** Multiple-loop refrigeration systems are widely used for the liquefaction of gases at low temperatures. In the liquefaction of natural gas, for example, two or three closed-loop refrigeration systems may be integrated to provide refrigeration in successively lower temperature ranges to cool and liquefy the feed gas. Typically, at least one of these closed-loop refrigeration systems uses a multi-component or mixed refrigerant which provides refrigeration in a selected temperature range as the liquid mixed refrigerant vaporizes and cools the feed gas by indirect heat transfer. Systems using two mixed refrigerant systems are well-known; in some applications, a third refrigerant system using a pure component refrigerant such as propane provides initial cooling of the feed gas. This third refrigerant system also may be used to provide a portion of the cooling to condense one or both of the mixed refrigerants after compression. Refrigeration in the lowest temperature range may be provided by a gas expander loop that is integrated with a mixed refrigerant loop operating in a higher temperature range.

**[0002]** In a typical multi-loop mixed refrigerant process for liquefying natural gas, the low level or coldest refrigeration loop provides refrigeration by vaporization in a temperature range of about –30°C to about –165°C to provide final liquefaction and optional subcooling of cooled feed gas. The refrigerant is completely vaporized in the coldest temperature range and may be returned directly to the refrigerant compressor, for example, as described in representative U.S. Patents 6,119,479 and 6,253,574 B1. Alternatively, the completely vaporized refrigerant may warmed before compression to provide precooling of the feed gas as described in U.S. Patents 4,274,849 and 4,755,200 or for cooling of refrigerant streams as described in Australian Patent AU-A-43943/85. A common characteristic feature of these typical liquefaction processes is that the refrigerant in the low level or coldest refrigeration loop is completely vaporized while providing refrigeration in the lowest temperature range. Any additional refrigeration provided by the refrigerant prior to compression thus is effected by the transfer of sensible heat from the vaporized refrigerant to other process streams.

**[0003]** US-A-4112700 discloses the liquefaction of natural gas by a process in which refrigerant to be vaporized in the coldest heat exchange zone is cooled in heat exchange zones providing lower level cooling of the natural gas and then in an auxiliary heat exchange zone in which a portion of the refrigerant is vaporized.

**[0004]** US-A-4057972 discloses, with reference to Fig. 4, the liquefaction of natural gas using three heat exchange zones. In the first and second zones, the natural gas feed is cooled by vaporizing propane at different pressures; the pressure in the second zone being higher than that in the first zone. The vaporized propane streams from these zones are compressed and condensed to provide a single liquid refrigerant stream from which the refrigeration load is rejected to air or water before separation into respective refrigerant streams for flashing to the first and second zones. The first zone chills the feed gas down to about 70°F (21°C) before drying and the second zone removes heavy hydrocarbons from the dried feed gas by cooling down to to about -40°F (-40°C). The hydrocarbon-freed feed gas is then liquefied in the third zone by vaporization of the lightest fraction of a multi-component refrigerant (MCR). The third zone is located at the cold end of a MCR cascade heat exchanger operating independently of the refrigerant cycle incorporating the first and second zones. MCR streams containing the lightest fraction are cooled in warmer parts of the cascade heat exchanger by vaporization of heavier MRC fractions.

**[0005]** In known liquefaction processes that use three integrated closed-loop refrigeration systems, the size of the process equipment in the third or lowest temperature refrigeration system may be smaller relative to the two warmer refrigeration systems. As the process liquefaction capacity is increased, the sizes of the compression and heat exchange equipment in the two warmer systems will reach the maximum sizes available from equipment vendors, while the sizes of the corresponding equipment in the lowest temperature refrigeration system will be smaller than the maximum sizes. In order to further increase the production capacity of this liquefaction process, parallel trains would be needed because of compression and/or heat exchanger size limitations in the two warmer refrigeration systems. It would be desirable to increase the maximum production capacity of this liquefaction process at the limits of available compressor and heat exchanger sizes, thereby allowing the use of larger single-train liquefaction processes.

## BRIEF SUMMARY OF THE INVENTION

**[0006]** This need is addressed by embodiments of the present invention, which relate to integrated refrigeration systems having increased production capacity without requiring duplicate parallel equipment for the warmer refrigeration systems.

**[0007]** The invention provides a method for liquefying a gas which comprises cooling a feed gas stream successively through first, second, and third temperature ranges to provide a liquefied product, wherein refrigeration for cooling the feed gas stream in the first temperature range is provided by a first vaporizing refrigerant, refrigeration for cooling the stream in the second temperature range is provided by a second vaporizing refrigerant, and refrigeration for cooling the stream in the third temperature range is provided by a third vaporizing refrigerant, said first, second and third refrigerants being of different compositions from each other,, and further wherein an auxiliary refrigerant derived from the third vaporizing refrigerant provides additional refrigeration by vaporization at temperatures above the lowest temperature in the second temperature range.

**[0008]** The auxiliary refrigerant can be a second portion of the third refrigerant vaporized at a different pressure.

**[0009]** The first pressure may be lower than the second pressure. The first refrigerant may be a single component refrigerant; the second and third refrigerants may be multi-component refrigerants. The first temperature range may be between about 35°C and about –70°C, the second temperature range may be between the temperatures of about 0°C and about –140°C, and the third temperature range may be between the temperatures of about –90°C and about –165°C. The feed gas stream may be natural gas.

**[0010]** The third refrigerant may be provided by

(1) compressing and cooling a vaporized refrigerant to provide an intermediate compressed refrigerant;

(2) combining the intermediate compressed refrigerant with an additional vaporized refrigerant to provide a combined intermediate refrigerant;

(3) compressing and cooling the combined intermediate refrigerant to provide a cooled compressed refrigerant; and

(4) further cooling and condensing the cooled compressed refrigerant to provide the third refrigerant, wherein the refrigeration for the cooling and

condensing is provided by vaporizing the second portion of the third refrigerant at the second pressure.

**[0011]** The cooling of the first compressed vapor may yield a two-phase stream, and the method may further comprise separating the two-phase stream into a vapor stream and a liquid stream, compressing the vapor stream to yield a further compressed vapor, pumping the liquid stream to provide a pressurized liquid, combining the further compressed vapor and the pressurized liquid to yield a combined refrigerant stream, and cooling the combined refrigerant stream to provide the cooled compressed refrigerant.

**[0012]** The auxiliary refrigerant can be derived from the third refrigerant other than as a portion thereof.

**[0013]** The first refrigerant may be a single component refrigerant. The second and third refrigerants may be multi-component refrigerants. The first temperature range may be between about 35°C and about –70°C, the second temperature range may be between about 0°C and about –140°C, and the third temperature range may be in the range of about –90°C and about –165°C. The feed gas stream may be natural gas.

**[0014]** The auxiliary refrigerant may be provided by

(1) partially or fully vaporizing the third refrigerant to provide a partially or fully vaporized warmed refrigerant; and

(2) combining the warmed refrigerant with a cooled reduced-pressure refrigerant to provide the auxiliary refrigerant;

wherein the cooled reduced-pressure refrigerant is provided by

(3) vaporizing the auxiliary refrigerant to yield a vaporized auxiliary refrigerant;

(4) compressing and cooling the vaporized auxiliary refrigerant to provide a cooled, compressed, partially-condensed auxiliary refrigerant;

(5) separating the cooled, compressed, partially-condensed auxiliary refrigerant into a liquid fraction and a vapor fraction;

(6) further cooling the liquid fraction by indirect heat exchange with the vaporizing auxiliary refrigerant to provide a cooled liquid refrigerant; and

(7) reducing the pressure of the cooled liquid refrigerant to provide the cooled reduced-pressure refrigerant.

**[0015]** The cooling of the first compressed vapor may yield a two-phase stream, and the method may further comprise separating the two-phase stream into a vapor stream and a liquid stream, compressing the vapor stream to yield a further compressed vapor, pumping the liquid stream to provide a pressurized liquid, combining the further compressed vapor and the pressurized liquid to yield a combined refrigerant stream, and

cooling the combined refrigerant stream to provide the cooled, compressed, partially condensed auxiliary refrigerant.

## BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS.

**[0016]** The following is a description by way of example only and with reference to the accompanying drawings of presently preferred embodiments of the invention:

**[0017]** Fig. 1 is a schematic flow diagram of a gas liquefaction and refrigeration system according to the prior art;

**[0018]** Fig. 2 is a schematic flow diagram of a gas liquefaction and refrigeration system according to an exemplary embodiment of the present invention utilizing two pressure levels for the vaporization of the coldest refrigerant;

**[0019]** Fig. 3 is a schematic flow diagram of a gas liquefaction and refrigeration system according to another exemplary embodiment of the present invention utilizing phase separation of the refrigerant used in the coldest temperature range;

**[0020]** Fig. 4 is a schematic flow diagram of a gas liquefaction and refrigeration system according to an alternative exemplary embodiment of the present invention; and

**[0021]** Fig. 5 is a schematic flow diagram of a gas liquefaction and refrigeration system according to an alternative exemplary embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

**[0022]** Embodiments of the invention described herein relate to improved refrigeration processes for gas liquefaction utilizing three closed-loop refrigeration systems that cool a feed stream through three temperature ranges at successively-decreasing temperatures. These embodiments are directed towards improvements to the refrigeration system that provides refrigeration in the lowest of these temperature ranges, wherein the sizes of the compressor and heat exchange equipment used in the refrigeration system in the lowest temperature range are increased relative to the sizes of the compressors and heat exchangers in the refrigeration systems used in the higher temperature ranges. The term refrigeration as used herein means the indirect transfer of heat at temperatures below ambient from a fluid stream to a refrigerant. A refrigerant is a pure or mixed fluid which absorbs heat from another stream by indirect heat exchange with that stream.

**[0023]** A schematic flow diagram of a representative prior art liquefaction process is given in Fig. 1. Feed gas in line 1, for example natural gas having been pretreated to remove water and other easily condensable impurities, is cooled through a first temperature range by indirect heat exchange with a first vaporizing refrigerant in first heat exchanger 3. The refrigerant may be a pure component refrigerant such as propane or alternatively may be a multi-component refrigerant comprising two or more light hydrocarbons selected from ethane, ethylene, propane, propylene, butane, and isobutane.

**[0024]** The cooled feed in line 5 is further cooled through a second temperature range by indirect heat exchange with a second vaporizing refrigerant in second heat exchanger 7. The further cooled feed in line 9 is still further cooled and liquefied through a third temperature range by indirect heat exchange with a third vaporizing refrigerant in third heat exchanger 11. The refrigerant typically is a multi-component refrigerant comprising two or more refrigerant components selected from methane, ethane, ethylene, propane, and propylene. Final liquefied product in line 13 may be reduced in pressure across expansion valve 15 to yield final liquid product in line 17.

**[0025]** Refrigeration for this process typically is provided by three nested or cascaded refrigeration systems. The first refrigeration system operates by supplying vapor refrigerant in line 101 to first compressor stage 103, wherein the gas is compressed to 2 to 4 bara (all pressures stated herein are absolute pressures), cooled in aftercooler 105, further compressed to 6 to 10 bara in second compressor 107, and cooled in aftercooler 109 to provide a compressed refrigerant at ambient temperature in line 111. The compressed refrigerant is further cooled and at least partially condensed in heat exchange passages in first heat exchanger 3. The partially or fully condensed refrigerant in line 113 is reduced in pressure across throttling valve 115 to provide reduced pressure refrigerant in line 117, and this refrigerant vaporizes in separate heat exchange passages to provide the refrigeration in first heat exchanger 3. Vaporized refrigerant in line 101 is compressed as described above.

**[0026]** The second refrigeration system operates by supplying vapor refrigerant in line 201 to compressor 203, wherein the gas is compressed to 10 to 20 bara and cooled in aftercooler 205 to approximately ambient temperature. The compressed refrigerant in line 207 is further cooled and at least partially condensed in heat exchange passages in first heat exchanger 3 and second heat exchanger 7. The partially or fully condensed refrigerant in line 209 is reduced in pressure across throttling valve 211 to provide reduced pressure refrigerant in line 213, and this refrigerant vaporizes in separate heat

exchange passages to provide the refrigeration in second heat exchanger 7. Vaporized refrigerant in line 201 is compressed as described above.

**[0027]** The third refrigeration system operates by supplying vapor refrigerant in line 301 to compressor 302, wherein the gas is compressed to about 35 to about 60 bara and cooled in aftercooler 303 to approximately ambient temperature. The compressed refrigerant in line 304 is further cooled and at least partially condensed in heat exchange passages in first heat exchanger 3, second heat exchanger 7, and third heat exchanger 11. The partially or fully condensed refrigerant in line 305 is reduced in pressure across throttling valve 307 to provide reduced pressure refrigerant in line 309, and this refrigerant vaporizes in separate heat exchange passages to provide the refrigeration in third heat exchanger 11. Vaporized refrigerant in line 301 is compressed as described above. The use of the third refrigeration loop including heat exchanger 11 and compressor 302 provides a portion of the total refrigeration duty needed to liquefy the feed gas and reduces the refrigeration duties and sizes of the first and second refrigeration systems.

**[0028]** Known modifications or alternatives to the prior art process using three refrigeration loops of Fig. 1 are possible. For example the first refrigeration loop may utilize cascade refrigeration in which the refrigerant is vaporized at three different pressures with the vaporized refrigerant returning to different stages in a multi-stage compressor. The second refrigeration loop may vaporize refrigerant at two different pressures through two separate sets of heat exchange passages in heat exchanger 7 and return each vaporized refrigerant stream to two separate compressor stages.

**[0029]** In another modification, the third refrigeration loop may vaporize refrigerant at two different pressures through two separate sets of heat exchange passages in heat exchanger 11 and return each vaporized refrigerant stream to two separate compressor stages. Vaporized refrigerant in line 301 prior to compressor 302 may be used in a separate heat exchanger to provide cooling for a portion of second refrigerant stream 215 and for a portion of compressed refrigerant in line 304.

**[0030]** In another known process with three refrigeration loops, vaporizing refrigerant in the first refrigeration loop is used to precool the feed gas; the first refrigeration loop compressor discharge is cooled and condensed by a portion of the vaporizing refrigerant from the second refrigeration loop. Vaporized refrigerant in the third refrigeration loop from the third heat exchanger prior to compression is used to further precool the feed gas. This further precooled feed gas then is cooled and condensed in the third heat

exchanger. The second refrigeration loop cools and condenses the compressed third refrigerant.

**[0031]** A common characteristic feature of these known liquefaction processes is that the refrigerant in the third refrigeration loop, i.e. the low level or coldest refrigeration loop, is completely vaporized while providing refrigeration in the lowest temperature range. Any additional refrigeration provided by the refrigerant prior to compression is effected only by the transfer of sensible heat from the vaporized refrigerant to other process streams.

**[0032]** Referring to the first exemplary embodiment of the invention shown in Fig. 2, feed gas in line 1, for example, natural gas having been pretreated to remove water and other condensable impurities, is cooled through a first temperature range by indirect heat exchange with a first vaporizing refrigerant in first heat exchanger 310. The refrigerant may be a multi-component refrigerant comprising, for example, two or more light hydrocarbons selected from ethane, ethylene, propane, butane, n-pentane, and i-pentane (i.e. 2-methyl butane). Alternatively, the refrigerant may be a single component such as propane. The upper temperature of the first temperature range may be ambient temperature and the lower temperature in the first temperature range may be between about –35°C and about –55°C. The specific refrigerant composition may be selected to achieve a desired lower temperature in the first temperature range.

**[0033]** The cooled feed in line 5 is further cooled through a second temperature range by indirect heat exchange with a second vaporizing refrigerant in second heat exchanger 311 to a temperature between about –40°C and about –100°C. The refrigerant typically is a multi-component refrigerant and may comprise, for example, two or more components selected from methane, ethane, ethylene, and propane. The specific refrigerant composition may be selected to achieve a desired lower temperature in the second temperature range.

**[0034]** The further cooled feed in line 9 is still further cooled and liquefied through a third temperature range, reaching a lower temperature between about –85°C and about –160°C, by indirect heat exchange with a third vaporizing refrigerant in third heat exchanger 312. This refrigerant is a multi-component refrigerant and may comprise, for example, two or more components selected from methane, ethane, ethylene, propane, propylene, one or more hydrocarbons having four carbon atoms, *n*-pentane, *i*-pentane (i.e. 2-methyl butane), and nitrogen. In this refrigerant, *i*-pentane is a preferred (but not required) component. The specific refrigerant composition may be selected to achieve a

desired lower temperature in the third temperature range. Final liquefied product in line 13 may be reduced in pressure across expansion valve 15 to yield final liquid product in line 17.

**[0035]** The first temperature range may be defined by a first temperature and a second temperature, and the first temperature may be ambient temperature. The second temperature range may be defined by the second temperature and a third temperature, and the third temperature range may be defined by the third temperature and a fourth temperature. The first temperature range is the highest or warmest temperature range and the third temperature range is the lowest or coldest temperature range. The first temperature is the highest temperature and the fourth temperature is the lowest temperature.

**[0036]** Refrigeration for this process may be provided by three nested or cascaded refrigeration systems. The first refrigeration system may be similar to the first refrigeration system as described above with reference to Fig. 1, and may operate by supplying vapor refrigerant in line 101 to first compressor stage 103, wherein the gas is compressed to 2 to 4 bara, cooled in aftercooler 105, further compressed to 6 to 10 bara in second compressor 107, and cooled in aftercooler 109 to provide a compressed refrigerant at ambient temperature in line 111. The compressed refrigerant is further cooled and at least partially condensed in heat exchange passages in first heat exchanger 310. The partially or fully condensed refrigerant in line 113 is reduced in pressure across throttling valve 115 to provide reduced pressure refrigerant in line 117, and this refrigerant vaporizes in separate heat exchange passages to provide the refrigeration in first heat exchanger 3. Vaporized refrigerant in line 101 is compressed as described above.

**[0037]** The second refrigeration system may be similar to the first refrigeration system as described above with reference to Fig. 1, and may operate by supplying vapor refrigerant in line 201 to compressor 203, wherein the gas is compressed to 10 to 20 bara and cooled in aftercooler 205 to approximately ambient temperature. The compressed refrigerant in line 207 is further cooled and at least partially condensed in heat exchange passages in first heat exchanger 310 and second heat exchanger 311. The partially or fully condensed refrigerant in line 209 is reduced in pressure across throttling valve 211 to provide reduced pressure refrigerant in line 213, and this refrigerant vaporizes in separate heat exchange passages to provide the refrigeration in second heat exchanger 311. Vaporized refrigerant in line 201 is compressed as described above.

**[0038]** The third refrigeration system of this embodiment departs from the prior art third refrigeration system described earlier and operates independently of the first and second refrigeration systems. In this third refrigeration system, condensed refrigerant in line 313 is reduced in pressure across throttling valve 314 and reduced-pressure condensed refrigerant from line 315 is vaporized in third heat exchanger 312 to provide refrigeration therein.

**[0039]** The reduced-pressure condensed refrigerant is totally vaporized in cold heat exchanger 312 and compressed at sub-ambient temperatures. A portion of the cooling of the compressed refrigerant is provided by autorefrigeration in a heat exchanger 357 at temperatures above the highest temperature of third heat exchanger 312 and above the lowest temperature of the feed stream in heat exchanger 311. The pressure of the vaporizing refrigerant in heat exchanger 357 is higher than the pressure of the vaporizing refrigerant in cold heat exchanger 312.

**[0040]** The vaporized refrigerant in line 316 is compressed to a pressure in the range of 3 to 25 bara in first compressor 359 and the compressed stream in line 361 is cooled to near ambient temperature in cooler 363 to provide intermediate compressed gas in line 365. The intermediate compressed gas is combined with a vaporized auxiliary refrigerant stream in line 367 (described below) and the combined refrigerant stream, typically at near ambient temperature and a pressure of 20 to 50 bara, is further compressed in second compressor 319, cooled and partially condensed in intercooler 320, and separated in separator 321 to provide a vapor stream in line 322 and a liquid stream in line 323.

**[0041]** The vapor stream in line 322 is further compressed to a pressure of 30 to 70 bara in compressor 324, the liquid stream 323 from separator 321 is pressurized by pump 325 to the same pressure, the two pressurized streams are combined to provide two-phase refrigerant stream 326, which is further cooled in aftercooler 327 by air or cooling water.

**[0042]** Partially or fully condensed refrigerant in line 328 is further cooled in heat exchanger 357 to provide cooled refrigerant in line 369 and this refrigerant stream is divided into first and second portions. The first portion is reduced in pressure across throttling valve 371 and the reduced-pressure refrigerant, which may be defined as an auxiliary refrigerant, flows via line 373 to heat exchanger 357, where it is warmed and vaporized to provide refrigeration therein and to yield the vaporized auxiliary refrigerant stream in line 367. The second portion of the cooled refrigerant flows via line 329 and is

further cooled in flow passages 356 of heat exchanger 312 to yield refrigerant 313 described above. Thus the auxiliary refrigerant in lines 367 and 373 is derived from the refrigerant in line 315 and in this embodiment has the same composition as the refrigerant in line 315.

**[0043]** Optionally, separator 321, pump 325, compressor 324, and cooler 327 are not used and the partially or fully condensed refrigerant in line 328 is provided directly from cooler 320.

**[0044]** Typically, the low pressure refrigerant stream in line 315 will be vaporized in a pressure range of about 2 to 10 bara in heat exchanger 312, while intermediate pressure refrigerant stream in line 373 will be vaporized at a higher pressure in a range of about 5 to 20 bara in heat exchanger 357.

**[0045]** When the above embodiment is used for the liquefaction of natural gas, hydrocarbons heavier than methane may be condensed and removed before final methane liquefaction by known methods including scrub columns or other partial condensation and/or distillation processes. These condensed natural gas liquids (NGLs) may be fractionated to provide selected components for the refrigerants in the refrigeration systems. Modifications to this embodiment may include provision for vaporizing a portion of the refrigerant in line 369 at a third higher pressure to provide warmer refrigeration than that provided by the lower pressure vaporizing refrigerant streams in lines 315 and 373.

**[0046]** The mixed refrigerant used in the third refrigerant system contains selected components and compositions that allow the refrigerant to vaporize over a broad temperature range. The criteria for selecting these components and the temperature range over which the refrigerant vaporizes are different than the criteria for selecting the mixed refrigerants typically used in the third or low level refrigeration loop of three-loop liquefaction systems known in the art. The mixed refrigerant in the third loop of the present invention should be capable of vaporizing in the third temperature range (i.e. in third heat exchanger 312) as well as at temperatures above the lowest temperature in the second temperature range (i.e. above the lowest temperature in second heat exchanger 311). Depending on the refrigerant composition and pressure, vaporization may be possible and desirable at temperatures above the highest temperature in the second temperature range.

**[0047]** Typical compositions (in mole %) of the refrigerant used in the third loop may include 5-15% nitrogen, 30-60% methane, 10-30% ethane, 0-10% propane, and 0-15%

*i*-pentane. One or more hydrocarbons having four carbon atoms may be present in the refrigerant, but preferably the total concentration of the one or more hydrocarbons having four carbon atoms is lower than the concentration of *i*-pentane. Subject to the vaporizing pressure, the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms in the refrigerant typically is greater than one and may be greater than 1.5. Normal pentane (*n*-pentane) also may be present in the refrigerant, preferably at lower concentrations than *i*-pentane.

**[0048]** The refrigeration components for use in the third refrigeration loop may be provided from hydrocarbon liquids heavier than methane that are condensed by initial cooling of a natural gas feed. These condensed natural gas liquids (NGLs) may be recovered and fractionated by known methods to obtain the individual components for use in the preferred mixed refrigerant. When the natural gas feed contains both *n*-pentane and *i*-pentane, for example, and when these components are recovered from NGLs by distillation for use in the refrigerant in the third refrigerant loop, the molar ratio of *i*-pentane to *n*-pentane in the refrigerant may be greater than the molar ratio of *i*-pentane to *n*-pentane in the feed gas. Preferably, the molar ratio of *i*-pentane to *n*-pentane in the refrigerant is greater than twice the molar ratio of *i*-pentane to *n*-pentane in the feed gas. *i*-pentane is preferred over *n*-pentane for use in this refrigerant because *i*-pentane has a lower freezing point than *n*-pentane, which allows the refrigerant to be used at lower temperatures.

**[0049]** When the natural gas feed contains both *i*-pentane and one or more hydrocarbons having four carbon atoms, and when these components are recovered from NGLs by distillation for use in the refrigerant in the third refrigerant loop, the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms in the refrigerant may be greater than the molar ratio of *i*-pentane to the one hydrocarbons having four carbon atoms in the feed gas.

**[0050]** The third refrigeration loop in this embodiment is self-refrigerated and is independent of the first and second refrigeration loops. In contrast with the process of Fig. 1, compressed refrigerant in the third refrigeration loop of Fig. 2 is not cooled in the first and second heat exchange zones by the first and second refrigeration loops. This unloads the first and second refrigeration loops, and thus reduces the sizes of the first and second heat exchange zones and the compression equipment in the first and second refrigeration loops compared to the process of Fig. 1. This is particularly beneficial when the process of Fig. 2 is used in a liquefaction system designed for a very large product throughput. When the sizes of the compression and heat exchange

equipment in the first and second refrigeration loops reach the maximum sizes available from equipment vendors, a higher production rate can be achieved with the process of Fig. 2 than with the process of Fig. 1.

**[0051]** Variations to the process embodiment of Fig. 2 are possible. For example, one stage or more than two stages of compression may be used as required, which would form multiple liquid streams for pumping in conjunction with the vapor compression stages. In another variation, the refrigerant composition and pressures in the compression system may be such that interstage condensation does not occur and vapor/liquid separation is not required.

**[0052/3]** Referring now to the exemplary embodiment of Fig. 3, the third refrigeration loop that provides refrigeration to cold heat exchanger 312 is modified to provide autorefrigeration by an internal auxiliary liquid refrigerant derived from the third refrigerant by phase separation. In the embodiment of Fig. 3, the feed stream in line 9 being liquefied is cooled to its final lowest temperature in this cold heat exchanger and reduced in pressure to provide liquid product in line 13, which may be reduced in pressure to provide a reduced-pressure product in line 17. The refrigeration for this final cooling is provided by cooling the refrigerant in line 329 to provide cooled liquid refrigerant in line 313, reducing the pressure across throttling valve 314 to yield reduced-pressure refrigerant in line 315, and partially or fully vaporizing this refrigerant to provide the refrigeration in heat exchanger 312.

**[0054]** The partially or fully vaporized refrigerant in line 316 is combined with a reduced-pressure refrigerant provided by pressure reduction across throttling valve 375 (described below) to yield a combined refrigerant stream in line 377. This combined refrigerant stream, which may be described as an auxiliary refrigerant stream, is warmed and vaporized in heat exchanger 379 to provide refrigeration therein and to generate vaporized auxiliary refrigerant in line 381. This vaporized auxiliary refrigerant is compressed in compressor 319, cooled and partially condensed in intercooler 320, and separated in separator 321 to provide a vapor stream in line 322 and a liquid stream in line 323.

**[0055]** The vapor stream in line 322 is further compressed to a pressure of 30 to 70 bara in compressor 324, the liquid stream from separator 321 is pressurized by pump 325 to the same pressure, the two pressurized streams are combined to provide two-phase refrigerant stream 326, which is further cooled in aftercooler 327 by air or cooling water to provide a partially condensed auxiliary refrigerant in line 328.

**[0056]** Optionally, separator 321, pump 325, compressor 324, and cooler 327 are not used and the partially condensed auxiliary refrigerant in line 328 is provided directly from cooler 320.

**[0057]** This partially condensed auxiliary refrigerant flows via line 328 to separator 330, where it is separated to yield a vapor refrigerant fraction in line 385 and a liquid refrigerant fraction in line 383. The liquid refrigerant fraction in line 383 is cooled in heat exchanger 379 to yield cooled refrigerant in line 389, which is reduced in pressure across throttling valve 375 and combined with partially or fully vaporized refrigerant in line 316 to yield the auxiliary refrigerant stream in line 377.

**[0058]** Thus the refrigerant in lines 383, 389, 377, and 381 is an auxiliary refrigerant derived from the refrigerant in line 315. In this embodiment, this auxiliary refrigerant contains the same components but has a different composition than the refrigerant in line 315. The different composition is a result of the phase separation of the partially condensed refrigerant in line 328 to yield the liquid refrigerant in line 387 and the vapor refrigerant in line 385.

**[0059]** Both embodiments illustrated in Figs. 2 and 3 differ from the prior art in that refrigerant from the third cooling loop that provides the lowest temperature of refrigeration is vaporized to provide refrigeration in temperature ranges both above and below the lowest temperature of the feed being cooled by the second cooling loop in heat exchanger 311. Thus refrigeration above the lowest temperature of the feed in heat

exchanger 311 is provided in heat exchanger 357 (Fig. 2) or 379 (Fig. 3) by vaporizing an auxiliary refrigerant derived from the refrigerant in line 315 that provides the refrigeration in coldest heat exchanger 312. Refrigeration below the lowest temperature of the feed being cooled in heat exchanger 311 is provided in heat exchanger 312. Thus the refrigeration in these two temperature ranges, i.e. both above and below the lowest temperature of the feed in heat exchanger 311, is provided by the third cooling loop.

**[0060]** Additionally, all or most of the refrigeration to cool the high pressure refrigerants in lines 383 and 385 after phase separation is provided by autorefrigeration in the third cooling loop, and this cooling of the compressed refrigerant in the third cooling loop is performed independently of the two warmer cooling loops. This feature is beneficial in that it greatly unloads the refrigeration requirements of the two warmer cooling loops, thereby allowing larger product capacities in natural gas liquefaction plants when the compressors in the two warmer cooling loops reach the maximum commercially available size.

**[0061]** Alternative embodiments of the exemplary processes of Figs. 2 and 3 are illustrated in Figs. 4 and 5 respectively. In these alternatives, the first refrigeration loop (compressors 103 and 107, coolers 105 and 109, and throttling valve 115) is replaced by a single-component cascade refrigeration system. Propane may be used as the single refrigerant in the first refrigeration loop. The second and third refrigeration loops remain unchanged from the embodiments of Figs. 2 and 3.

**[0062]** Multi-stage compressor 119 and aftercooler 121 are operated to provide compressed refrigerant in line 123 at near ambient temperature and a pressure in the range of 10 to 15 bara. The compressed refrigerant inline 123 is reduced in pressure across throttling valve 125 and the reduced-pressure refrigerant in line 127 is partially vaporized in heat exchanger 129 to provide refrigeration therein and yield a two-phase refrigerant in line 131. This two-phase refrigerant is separated in separator 133 to provide vapor in line 135, which vapor is returned to a lower pressure stage suction of compressor 119, and liquid in line 137. This liquid is reduced in pressure across throttling valve 139 and is partially vaporized in heat exchanger 129 to provide refrigeration therein. Two-phase refrigerant in line 141 is separated in separator 143 to yield vapor in line 145, which vapor is returned to an intermediate stage suction of compressor 119, and liquid in line 147. This liquid is reduced in pressure across throttling valve 149 and the reduced-pressure refrigerant is vaporized in heat exchanger 129 to provide additional refrigeration therein. Vapor in line 151 is returned to the inlet of compressor 119.

**[0063]** Any of the embodiments of Figs. 2 to 5 may be installed as a retrofit to an existing two-loop dual mixed refrigerant liquefaction plant or two-loop propane-mixed refrigerant natural gas liquefaction plant.

## EXAMPLE

**[0064]** The process of Fig. 3 is illustrated by the following non-limiting example in which a feed gas stream of 100 kg-moles/hour of natural gas in line 1 is liquefied to provide a liquefied natural gas (LNG) product in line 17. The feed gas in line 1, having been purified previously (not shown) to remove water and acid gas impurities, is provided at a temperature of 27°C and a pressure of 60 bara. The feed gas in line 1 and mixed refrigerant vapor in line 207 are cooled to a temperature of –39°C in first heat exchanger 130 by a vaporizing mixed refrigerant having a molar composition of 2% methane, 62% ethane and 34% isobutane plus butane.. To effect this cooling, mixed refrigerant stream 113 is vaporized and warmed in heat exchanger 310 before being fed to compressor 103 at a pressure of 5 bara. Compressor 103 has a discharge pressure of 19.5 bara. The mixed refrigerant is cooled to a temperature of 36.5°C and condensed in aftercooler 105 using an ambient temperature cooling medium such as cooling water or air. The resulting stream is further compressed in compressor 107 to a pressure of 34 bar and cooled in aftercooler 109 to 36.5°C using an ambient temperature cooling medium such as cooling water or air Total mixed refrigerant flow in line 113 is 124 kg-mole/hour.

**[0065]** The cooled feed in line 5 and second mixed refrigerant in line 208 are cooled to a temperature of –119°C in second heat exchanger 311 to yield further cooled feed in line 9 and further cooled second mixed refrigerant in line 209. The mixed refrigerant in line 209 is throttled across valve 211 to a pressure of 4.2 bara to yield a reduced-pressure mixed refrigerant in line 213. The mixed refrigerant in line 213 is vaporized in heat exchanger 311 to provide refrigeration therein. The mixed refrigerant for this second cooling loop has a flow rate of 87 kg moles/hour and a composition of 27 mole% methane, 63 mole% ethane and 10 mole% propane. The vaporized second mixed refrigerant stream in line 201 is compressed in three-stage intercooled compressor 203 to a pressure of 57 bara. The compressed mixed refrigerant is cooled in aftercooler 205 to 36.5°C using cooling water to provide cooled compressed mixed refrigerant in line 207.

**[0066]** Feed in line 9 and third mixed refrigerant in line 329 are cooled to a final temperature of –156°C in third heat exchanger 312 to yield, respectively, LNG product in line 17 and condensed third mixed refrigerant in line 313. The mixed refrigerant in line 313 is throttled across valve 314 to a pressure of 3.7 bara to provide reduced-pressure third mixed refrigerant in line 315. This reduced-pressure third mixed refrigerant partially vaporizes in third heat exchanger 312 to provide refrigeration therein and a partially vaporized refrigerant in line 316, having a vapor fraction of 95% and a temperature of –123°C. The mixed refrigerant for this third cooling loop in line 329 has a flow rate of 59 kg-moles/hour and a composition (in mole %) of 12% nitrogen, 52% methane, 18% ethane, 6% propane, and 12% *i*-pentane.

**[0067]** Mixed refrigerant in line 389 is throttled in 375 to a pressure of about 3.6 bara and combined with stream 316 to form stream 377 which is fully vaporized and warmed to 26°C in fourth heat exchanger 379 to provide refrigeration therein. Vaporized refrigerant in line 381 is compressed to 17.7 bara in first stage compressor 319, cooled to 36.5°C and partially liquefied in ambient air or water-cooled intercooler 320. The two-phase refrigerant is separated in separator 321 to yield refrigerant vapor in line 322 and refrigerant liquid in line 323. The refrigerant liquid is pressurized in pump 325 to 47 bara. Refrigerant vapor in line 322 is compressed to a pressure of 47 bara in compressor 324, combined with the pressurized refrigerant from pump 325, and the combined stream in line 326 is cooled in water-cooled aftercooler 327 to 36.5°C to yield cooled mixed refrigerant in line 328. The two-phase refrigerant is separated in separator 330 to yield mixed refrigerant vapor in line 385 and mixed refrigerant liquid in line 383. The mixed refrigerant liquid is cooled in fourth heat exchanger 379 to provide cooled mixed refrigerant in line 389 The mixed refrigerant vapor is cooled and liquefied in fourth heat exchanger 379 to provide cooled mixed refrigerant in line 329, which is further cooled in third heat exchanger 312 as earlier described.

**[0068]** In the above description of Figs. 1-5, reference numbers for lines (i.e. pipes through which process streams flow) also may refer to the process streams flowing in those lines. In the following method claims, reference numbers denote process streams flowing in those lines. In the following system claims, the reference numbers denote the lines rather than the process streams flowing in these lines. Reference numbers from Figs. 2-5 are included in the following claims for clarity and are not meant to limit the scope of the claims in any way.

## CLAIMS

1. A method for liquefying a gas (1) which comprises cooling a feed gas stream successively through three heat exchange zones (310, 311 & 312) at respective first, second, and third temperature ranges to provide a liquefied product (13), wherein refrigeration for cooling the feed gas stream in the first temperature range is provided by a first vaporizing refrigerant (117), refrigeration for cooling the stream in the second temperature range is provided by a second vaporizing refrigerant (213), and refrigeration for cooling the stream in the third temperature range is provided by a third vaporizing refrigerant (315), said first, second and third refrigerants being of different compositions from each other, characterized in that additional refrigeration is provided by vaporization (357; 379), at temperatures above the lowest temperature in the second heat exchange zone (311), of an auxiliary refrigerant (373, 377) derived from said third vaporizing refrigerant (315) vaporized in the third (coldest) heat exchange zone (312).

2. A method of Claim 1, wherein the auxiliary refrigerant (373) is of the same composition as the refrigerant (315) vaporized in said coldest heat exchange zone (312) but is vaporized (357) at a different pressure.

3. A method of Claim 2, wherein the refrigerant (315) for said coldest heat exchange zone (312) is provided by

(1) compressing (359) and cooling (363) a vaporized refrigerant (316) to provide an intermediate compressed refrigerant (365);

(2) combining the intermediate compressed refrigerant (363) with the vaporized auxiliary refrigerant (367) to provide a combined intermediate refrigerant;

(3) compressing (319) and cooling (320) the combined intermediate refrigerant to provide a cooled compressed refrigerant (328); and

(4) further cooling and condensing (357) the cooled compressed refrigerant (328) by indirect heat exchange with vaporizing auxiliary refrigerant (373) to provide a combined refrigerant (369), one portion (329) of which provides the refrigerant (315) for said coldest heat exchange zone (312) and another portion of which provides the auxiliary refrigerant (373).

4. A method of Claim 1, wherein the auxiliary refrigerant (377) is of a different composition from the refrigerant (315) vaporized in said coldest heat exchange zone (312)

5. A method of Claim 4, wherein the auxiliary refrigerant (377) is provided by

(1) partially or fully vaporizing the refrigerant (315) in said coldest heat exchange zone (312) to provide a partially or fully vaporized warmed refrigerant (316); and

(2) combining the warmed refrigerant (316) with a cooled reduced-pressure (375) refrigerant to provide the auxiliary refrigerant (377); and wherein said cooled reduced-pressure refrigerant is provided by

(3) vaporizing (379) the auxiliary refrigerant (377) to yield a vaporized auxiliary refrigerant (381);

(4) compressing (319) and cooling (320) the vaporized auxiliary refrigerant to provide a cooled, compressed, partially-condensed auxiliary refrigerant (328);

(5) separating (330) the cooled, compressed, partially-condensed auxiliary refrigerant (328) into a liquid fraction (383) and a vapor fraction (385);

(6) further cooling the liquid fraction (383) by indirect heat exchange (379) with the vaporizing auxiliary refrigerant (377) to provide a cooled liquid refrigerant (389); and

(7) reducing the pressure (375) of the cooled liquid refrigerant (389) to provide the cooled reduced-pressure (375) refrigerant.

6. A method of any one of the preceding claims, wherein the feed gas stream (1) is natural gas.

7. A method of any one of the preceding claims, wherein the first refrigerant is a single or multi- component refrigerant and the second and third refrigerants are respective multi-component refrigerants.

8. A method of any one of the preceding claims, wherein the first, second and third refrigeration system are separate closed loop systems.

9. A method of any one of the preceding claims, wherein said first heat exchange zone (310) cools the feed gas stream to between -35°C and -55°C, said

second heat exchange zone (311) cools the feed gas stream to between -40°C and -100°C, and said third heat exchange zone (312) cools the feed gas stream to between -85°C and -160°C.

10. A system for liquefying a gas stream (1) by a method of Claim 1, which system comprises three heat exchange zones (310, 311 & 312) for cooling the gas stream (1) successively through first, second and third respective temperature ranges to provide a liquefied product (13) and respective refrigeration systems for providing respective first, second and third refrigerants (117, 213 & 315) of different compositions to each other to said heat exchange zones (310, 311 & 312), characterized in that a further heat exchange zone (357; 379) is present to vaporize, at temperatures above the lowest temperature of the second heat exchange zone (311), an auxiliary refrigerant (373, 377) derived from said third refrigerant (315) vaporized in the third (coldest) heat exchange zone (312).

11. A system of Claim 10, wherein the auxiliary refrigerant (373) is of the same composition as the refrigerant (315) vaporized in said coldest heat exchange zone (312) but is vaporized in said further heat exchange zone (357) at a different pressure.

12. A system of Claim 10 or Claim 11, comprising

means for compressing (359) and cooling (363) a vaporized refrigerant (316) to provide an intermediate compressed refrigerant (365);

means for combining the intermediate compressed refrigerant (363) with the vaporized auxiliary refrigerant (367) to provide a combined intermediate refrigerant; and

means for compressing (319) and cooling (320) the combined intermediate refrigerant to provide a cooled compressed refrigerant (328);

and wherein said further heat exchange means (357) further cools and condenses the cooled compressed refrigerant (328) by indirect heat exchange with vaporizing auxiliary refrigerant (373) to provide a combined refrigerant (369), one portion (329) of which provides the refrigerant (315) for said coldest heat exchange zone (312) and another portion of which provides the auxiliary refrigerant (373),.

13. A system of Claim 10 or Claim 11, wherein the auxiliary refrigerant (377) is vaporized in said further heat exchanger to yield a vaporized auxiliary refrigerant (381) and the system comprises:

means for combining partially or fully vaporized warmed refrigerant (316) from the coldest heat exchange zone (312) with a cooled reduced-pressure (375) refrigerant to provide the auxiliary refrigerant (377);

means for compressing (319) and cooling (320) the vaporized auxiliary refrigerant to provide a cooled, compressed, partially-condensed auxiliary refrigerant (328);

means for separating (330) the cooled, compressed, partially-condensed auxiliary refrigerant (328) into a liquid fraction (383) and a vapor fraction (385);

means for further cooling the liquid fraction (383) by indirect heat exchange (379) with the vaporizing auxiliary refrigerant (377) to provide a cooled liquid refrigerant (389); and

means (375) for reducing the pressure of the cooled liquid refrigerant (389) to provide the cooled reduced-pressure (375) refrigerant.