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] 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.

[0004] 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. This need is addressed by the present invention, which provides an integrated refrigeration system having increased production capacity without requiring duplicate parallel equipment for the warmer refrigeration systems.

BRIEF SUMMARY OF THE INVENTION

[0005] In one aspect, the present invention provides a method for liquefying a gas which comprises cooling a feed gas stream successively through at least two heat exchange zones at respective temperature ranges to provide a liquefied product, wherein refrigeration for cooling the feed gas stream in said temperature ranges is provided by respective vaporizing refrigerants, characterized in that the refrigerant in the coldest temperature range is only partially vaporized in the coldest heat exchange zone and the partially vaporized refrigerant is further vaporized in a heat exchange zone at temperatures above the highest temperature of the coldest heat exchange zone.

[0006] In one embodiment, the invention relates to a method for liquefying a gas which comprises cooling a feed gas stream successively through first and second temperature ranges to provide a liquefied product, wherein refrigeration for cooling the feed gas stream in the first temperature range is provided by a vaporizing first refrigerant and refrigeration for cooling the feed gas stream in the second temperature range is provided by a vaporizing second refrigerant and said second refrigerant provides additional refrigeration by further vaporization at temperatures above the lowest temperature in the first temperature range.

[0007] In another embodiment, the invention relates to 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 vaporizing first refrigerant, refrigeration for cooling the feed gas stream in the second temperature range is provided by a vaporizing second refrigerant, and refrigeration for cooling the feed gas stream in the third temperature range is provided by a vaporizing third refrigerant and said third refrigerant provides additional refrigeration by further vaporization at temperatures above the lowest temperature in the second temperature range. The first refrigerant may be a single component refrigerant. The second and third refrigerants may be multi-component refrigerants.

[0008] 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 between about -90°C and about -165°C. The feed gas stream may be natural gas.

[0009] The cooling of the feed gas stream may be effected by:

(a) cooling the feed gas stream in the first temperature range by indirect heat exchange with the first refrigerant vaporizing in a first heat exchange zone to provide a first partially cooled feed stream and a first refrigerant vapor;

(b) further cooling the partially cooled feed stream in the second temperature range by indirect heat exchange with the second refrigerant vaporizing in a second heat exchange zone to provide a second partially cooled feed stream and a second refrigerant vapor; and

(c) further cooling the second partially cooled feed stream in the third temperature range by indirect heat exchange with the third refrigerant vaporizing in a third heat exchange zone to provide the liquefied product (13) and a two-phase refrigerant stream.

[0010] The third refrigerant may be a multi-component mixture comprising two or more components selected from nitrogen and hydrocarbons having from one to five carbon atoms. The third refrigerant may comprise (in mole %) 5-15% nitrogen, 30-60% methane, 10-30% ethane, 0-10% propane, and 5-15% *i*-pentane. The third refrigerant may comprise *i*-pentane and one or more hydrocarbons having four carbon atoms, wherein the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms is greater than one.

[0011] The third refrigerant may comprise *i*-pentane and *n*-pentane and the molar ratio of *i*-pentane to *n*-pentane in the third refrigerant may be greater than one. The *i*-pentane and *n*-pentane may be obtained from the feed gas stream and the molar ratio of *i*-pentane to *n*-pentane in the third refrigerant may be greater than the molar ratio of *i*-pentane to *n*-pentane in the feed gas stream. The third refrigerant may comprise *i*-pentane and one or more hydrocarbons having four carbon atoms, wherein the *i*-pentane and one or more hydrocarbons having four carbon atoms in the third refrigerant may be obtained from the feed gas stream, and wherein the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms in the third refrigerant may be greater than the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms in the feed gas stream.

[0012] The third refrigerant may be provided in a third recirculating refrigeration process that comprises vaporizing the two-phase refrigerant stream in a fourth heat exchange zone at temperatures greater than a lowest temperature in the second temperature range to provide a third refrigerant vapor, compressing the third refrigerant vapor to yield a compressed third refrigerant stream, cooling the compressed third refrigerant stream in the fourth heat exchange zone by indirect heat exchange with the two-phase refrigerant stream to provide a cooled third refrigerant stream, and further cooling the cooled third refrigerant stream to provide the third refrigerant in (c).

[0013] The further cooling of the cooled third refrigerant stream may be effected by indirect heat exchange with the third refrigerant vaporizing in the third heat exchange zone. The compressed third refrigerant stream may be provided by compressing the third refrigerant vapor in a first compression stage to provide a first compressed vapor, cooling the first compressed vapor to yield a two-phase stream, 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 compressed third refrigerant stream.

[0014] The third refrigerant may be provided in a third recirculating refrigeration process that comprises vaporizing the two-phase refrigerant stream in a fourth heat exchange zone at temperatures greater than a lowest temperature in the second temperature range to provide a third refrigerant vapor, compressing and cooling the third refrigerant vapor to yield a compressed third refrigerant stream, cooling the compressed third refrigerant stream in the first heat exchange zone by indirect heat exchange with

the first vaporizing refrigerant and in the fourth heat exchange zone by indirect heat exchange with the vaporizing two-phase refrigerant stream to provide a cooled third refrigerant stream, and further cooling the cooled third refrigerant stream to provide the third refrigerant in (c).

[0015] The third refrigerant may be provided in a third recirculating refrigeration process that comprises combining the two-phase refrigerant stream with a cooled reduced-pressure liquid refrigerant stream to provide a combined two-phase refrigerant stream, vaporizing the combined refrigerant stream in a fourth heat exchange zone at temperatures greater than a lowest temperature in the second temperature range to provide a third refrigerant vapor, compressing and cooling the third refrigerant vapor to provide a partially-condensed third refrigerant, separating the partially-condensed third refrigerant into a refrigerant vapor stream and a refrigerant liquid stream, compressing and cooling the refrigerant vapor stream to form a partially-condensed stream and separating the partly-condensed stream into a compressed third refrigerant vapor and a liquid refrigerant, reducing the pressure of the liquid refrigerant to provide a reduced-pressure liquid refrigerant, combining the reduced-pressure liquid refrigerant with the refrigerant liquid stream to provide a combined refrigerant liquid, subcooling the combined refrigerant liquid stream in the fourth heat exchange zone to provide a subcooled liquid refrigerant, combining the subcooled liquid refrigerant and the two-phase refrigerant stream to provide a combined two-phase refrigerant, vaporizing the combined two-phase refrigerant in the fourth heat exchange zone to provide refrigeration therein, cooling compressed third refrigerant vapor in the fourth heat exchange zone to provide a cooled third refrigerant stream, and further cooling and reducing the pressure of the cooled third refrigerant stream to provide the third refrigerant.

[0016] In a second aspect of the present invention, there is provided a system for liquefying a gas stream by a method of the aforementioned method aspect, which system comprises at least two heat exchange zones for cooling the gas stream successively through respective temperature ranges to provide a liquefied product, respective refrigeration systems for providing respective refrigerants in respective refrigerant lines to the heat exchange zones, characterized in that the coldest temperature heat exchange zone only partially vaporizes the respective (i.e. coldest) refrigerant and the respective refrigeration system providing the coldest refrigerant comprises a further heat exchange zone to further vaporize the resultant partially vaporized refrigerant at temperatures above the highest temperature of the coldest heat

exchange zone. Usually, there will be only two or, preferably, three heat exchange zones through which the gas stream successively passes for liquefaction.

[0017] An embodiment of the second aspect of the invention relates to a system for liquefying a gas stream which comprises first, second, and third heat exchange zones for cooling the gas stream successively through first, second, and third temperature ranges, respectively, to provide a liquefied product, a first refrigeration system for providing a first refrigerant in a first refrigerant line to the first heat exchange zone, a second refrigeration system for providing a second refrigerant in a second refrigerant line to the second heat exchange zone, and a third refrigeration system for providing a third refrigerant in a third refrigerant line to the third heat exchange zone, wherein the third refrigeration system comprises piping means (318) to provide a vaporized third refrigerant to compression means for compressing the vaporized third refrigerant, piping means to provide a compressed third refrigerant to a fourth heat exchange zone, piping means for providing a cooled compressed third refrigerant from the fourth heat exchange zone to the third heat exchange zone, means to further cool the cooled compressed third refrigerant in the third heat exchange zone to provide a condensed third refrigerant, and pressure reduction means to reduce the pressure of the condensed third refrigerant to provide the third refrigerant to the third refrigerant line and the third heat exchange zone.

[0018] The compression means for compressing the vaporized third refrigerant may comprise a first stage compressor, an intercooler to cool and partially condense a first compressed refrigerant stream to yield a partially condensed first compressed refrigerant stream, a separator to separate the partially condensed first compressed refrigerant stream into a vapor refrigerant stream and a liquid refrigerant stream, a second stage compressor to compress the vapor refrigerant stream to provide a compressed vapor refrigerant stream, a pump to pressurize the liquid refrigerant stream to provide a pressurized liquid refrigerant stream, piping means to combine the compressed vapor refrigerant stream and the pressurized liquid refrigerant stream and provide a combined refrigerant stream to an aftercooler to cool the combined refrigerant stream to provide the compressed third refrigerant.

[0019] The fourth heat exchange zone may include means for subcooling a refrigerant liquid to provide a subcooled refrigerant liquid, pressure reduction means for reducing the pressure of the subcooled refrigerant liquid to provide a reduced-pressure refrigerant, piping means for combining the reduced-pressure refrigerant with the further vaporizing third refrigerant from the third heat exchange zone to provide a combined vaporizing refrigerant stream to the fourth heat zone, wherein the combined vaporizing refrigerant

stream vaporizes in the fourth heat exchange zone to provide the vaporized third refrigerant.

[0020] The compression means for compressing the vaporized third refrigerant may comprise a first stage compressor, an intercooler to cool and partially condense a first compressed refrigerant stream to yield a partially condensed first compressed refrigerant stream, a first separator to separate the partially condensed first compressed refrigerant stream into a first vapor refrigerant stream and a first liquid refrigerant stream, a second stage compressor to compress the vapor refrigerant stream to provide a compressed vapor refrigerant stream, an aftercooler to cool the compressed vapor refrigerant stream to provide a cooled two-phase refrigerant stream, a second separator to provide a second liquid refrigerant stream and the compressed third refrigerant, pressure reduction means to reduce the pressure of the second liquid refrigerant stream to provide a reduced-pressure second liquid refrigerant stream, and piping means to combine the reduced-pressure second liquid refrigerant stream and the first liquid refrigerant stream to provide the refrigerant liquid to the fourth heat exchange zone.

[0021] In another embodiment, the invention relates to a system for liquefying a gas stream which comprises first, second, and third heat exchange zones for cooling the gas stream successively through first, second, and third temperature ranges, respectively, to provide a liquefied product, a first refrigeration system for providing a first refrigerant vaporizing in the first heat exchange zone, a second refrigeration system for providing a second refrigerant vaporizing in the second heat exchange zone, and a third refrigeration system for providing a third refrigerant vaporizing in the third heat exchange zone, wherein the third refrigeration system comprises compression means for compressing a vaporized third refrigerant to provide a compressed third refrigerant, cooling means in the first heat exchange zone for cooling the compressed third refrigerant by indirect heat exchange with the first refrigerant vaporizing in the first heat exchange zone to provide a cooled compressed third refrigerant, a fourth heat exchange zone to further cool the cooled compressed third refrigerant by indirect heat exchange with a vaporizing third refrigerant from the third heat exchange zone to provide the vaporized third refrigerant and a further cooled compressed third refrigerant, means to further cool the cooled compressed third refrigerant in the third heat exchange zone to provide a condensed third refrigerant, and pressure reduction means to reduce the pressure of the condensed third refrigerant to provide the third refrigerant vaporizing in the third heat exchange zone.

[0022] In a related embodiment, the invention includes a refrigerant comprising *i*-pentane, one or more hydrocarbons having four carbon atoms, and one or more components selected from nitrogen, methane, ethane, ethylene, propane, and propylene, wherein the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms is greater than one. The refrigerant also may contain *n*-pentane and the molar ratio of *i*-pentane to *n*-pentane may be greater than one. The refrigerant may have a composition comprising (in mole %) 5-15% nitrogen, 30-60% methane, 10-30% ethane, 0-10% propane, and 5-15% *i*-pentane.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0023] The following is a description by way of example only and with reference to the accompanying drawings of presently preferred embodiments of the invention.

[0024] Fig. 1 is a schematic flow diagram of a gas liquefaction and refrigeration system according to the prior art;

[0025] Fig. 2 is a schematic flow diagram of a gas liquefaction and refrigeration system according to an exemplary embodiment of the present invention;

[0026] Fig. 3 is a schematic flow diagram of a gas liquefaction and refrigeration system according to an alternative exemplary embodiment of the present invention;

[0027] Fig. 4 is a schematic flow diagram of a gas liquefaction and refrigeration system according to another exemplary embodiment of the present invention and

[0028] Fig. 5 is a schematic flow diagram of a gas liquefaction and refrigeration system according to another alternative exemplary embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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 bar (all pressures stated herein are absolute pressures), cooled in aftercooler 105, further compressed to 6 to 10 bar 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.

[0033] The second refrigeration system operates by supplying vapor refrigerant in line 201 to compressor 203, wherein the gas is compressed to 10 to 20 bar 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.

[0034] The third refrigeration system operates by supplying vapor refrigerant in line 301 to compressor 302, wherein the gas is compressed to 35 to 60 bar 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.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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.

[0039] In the several embodiments of the present invention, the condensed refrigerant of the third or coldest refrigeration loop is only partially vaporized in the third heat exchanger in the third or lowest temperature range. The partially vaporized refrigerant from the third heat exchanger is further vaporized at temperatures above the lowest temperature in the second temperature range. This is illustrated by a 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.

[0040] 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.

[0041] 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.

[0042] 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.

[0043] 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 bar, cooled in aftercooler 105, further compressed to 6 to 10 bar 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.

[0044] 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 bar

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.

[0045] 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 partially vaporized in third heat exchanger 312 to provide refrigeration therein. Partially-vaporized refrigerant flows through line 316 and vaporizes completely in fourth heat exchanger 317 to provide refrigeration therein. Vaporized refrigerant in line 318, typically at near ambient temperature and a pressure of 2 to 10 bar is compressed in first 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.

[0046] The vapor stream in line 322 is further compressed to a pressure of 30 to 70 bar in compressor 324, the liquid stream in line 232 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. Partially or fully condensed refrigerant in line 328 is further cooled in fourth heat exchanger 317 to provide cooled refrigerant in line 329. The cooled refrigerant in line 329 is further cooled in flow passages 356 of third heat exchanger 312 to yield refrigerant 313 described above.

[0047] 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.

[0048] 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 5-15% *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. 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.

[0049] 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.

[0050] 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.

[0051] 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.

[0052] 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.

[0053] In an alternative embodiment of the process of Fig. 2, the second refrigeration system is not required, and heat exchanger 311, valve 211, compressor 203, cooler 205, and the associated piping are not used. In this alternative, heat exchanger 310 would not include passages for cooling refrigerant supplied via line 207. The process in this embodiment therefore comprises cooling the feed gas in line 1 successively through first and second temperature ranges to provide a liquefied product in line 13, wherein refrigeration for cooling the gas stream is provided by a first refrigerant in line 117 vaporizing in the first temperature range and a second refrigerant in line 315 vaporizing in the second temperature range and further vaporizing at temperatures above a lowest temperature in the first temperature range. Thus the temperature ranges in which the first and second refrigerants vaporize overlap. In this alternative embodiment, the first refrigerant may be propane and the second refrigerant may be a multi-component refrigerant. In another version of this embodiment, both refrigerants may be selected multi-component refrigerants.

[0054] An alternative embodiment of the exemplary process of Fig. 2 is illustrated in Fig. 3. In this alternative, the first refrigeration loop of Fig. 2 (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. In this embodiment, the second and third refrigeration loops remain unchanged from the embodiment of Fig. 2.

[0055] 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 bar. 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.

[0056] Another alternative to the exemplary embodiment of Fig. 2 is illustrated in Fig. 4. In this embodiment, a modified third refrigeration loop is used wherein liquid formed in the compression step is combined with partially vaporized liquid from the third heat exchanger and the combined stream provides the refrigeration to cool the compressed refrigerant vapor. Vaporized refrigerant in line 330 is compressed in compressor 331 to 2 to 10 bar, cooled and partially condensed in aftercooler 332, and separated in separator 333 to provide vapor in line 334 and liquid in line 335. The vapor in line 334 is further compressed in compressor 336 to 6 to 20 bar, cooled and partially condensed in aftercooler 337, and separated in separator 338 to provide vapor in line 339 and liquid in line 340.

[0057] The liquid in line 340 is reduced in pressure across throttling valve 341, the reduced-pressure liquid in line 342 is combined with the liquid from line 335, and the combined liquid in line 343 is subcooled in fourth heat exchanger 344 to yield a subcooled liquid refrigerant in line 345. This subcooled refrigerant is reduced in pressure across throttling valve 346 and combined with partially-vaporized refrigerant in line 316 from third heat exchanger 312. The combined refrigerant in line 347 is vaporized in heat exchanger 344 to provide refrigeration therein and yield refrigerant vapor in line 330. Cooled refrigerant in line 329 is further cooled and at least partially liquefied in third heat exchanger 312, reduced in pressure across throttling valve 314 to provide reduced-pressure refrigerant in line 315, wherein the reduced-pressure refrigerant is partially

vaporized in heat exchanger 312 to provide refrigeration therein as described above. Partially-vaporized refrigerant in line 316 returns to heat exchanger 344 as described above.

[0058] Another alternative to the exemplary embodiment of Fig. 2 is illustrated in Fig. 5. In this exemplary embodiment, a modified third refrigeration loop is used wherein the refrigerant is compressed at sub-ambient temperatures and a portion of the cooling of the compressed refrigerant is provided by the first refrigeration loop. Referring to Fig. 5, refrigerant vapor in line 348 at a temperature in the range of about 0°C to about -90°C is compressed in compressor 349 to 10 to 20 bar and cooled in aftercooler 350 to ambient temperature. Cooled compressed refrigerant in line 351 is further cooled in flow passages 352 of first heat exchanger 352, wherein refrigeration is provided by the first refrigeration loop as earlier described.

[0059] Cooled refrigerant in line 354 is further cooled in fourth heat exchanger 355 to provide a further cooled refrigerant in line 329. Cooled refrigerant in line 329 is further cooled and at least partially liquefied in third heat exchanger 312, reduced in pressure across throttling valve 314 to provide reduced-pressure refrigerant in line 315, wherein the reduced-pressure refrigerant is partially vaporized in heat exchanger 312 to provide refrigeration therein as described above. Partially-vaporized refrigerant in line 316 returns to heat exchanger 354 as described above.

[0060] In this alternative embodiment, mixed refrigerant in line 348 is at a temperature in the range of about 0 to about -90°C at the inlet to compressor 349. The use of cold compression in compressor 349 contrasts with the embodiments of Figs. 2, 3, and 4, wherein the refrigerant vapor enters the compressor inlet at approximately ambient temperature. The mixed refrigerant in the embodiment of Fig. 5 is lighter than the refrigerant in the embodiment of Fig. 2; preferably, the mixed refrigerant of Fig. 5 contains no components heavier than propane.

[0061] When the above embodiments are 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. As described above, these condensed natural gas liquids (NGLs) may be fractionated to provide selected components for the refrigerants in the refrigeration systems.

EXAMPLE

[0062] 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 bar. The feed gas in line 1 and mixed refrigerant vapor in line 207 are cooled to a temperature of -33°C in first heat exchanger 129 by three stages of propane cooling. To effect this cooling, propane is evaporated at three pressure levels forming three suction streams (135,145, and 151) to propane compressor 119. The pressures of the three suction streams are 1.3 bar, 2.8 bar, and 4.8 bar respectively. Compressor 119 has a discharge pressure of 16.3 bar. The propane is cooled to a temperature of 43°C and condensed in aftercooler 121 using an ambient temperature cooling medium such as cooling water or air. Total propane flow in line 123 is 114 kg-mole/hour.

[0063] 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 bar 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 bar. 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.

[0064] 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 bar 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 the partially-vaporized refrigerant in line 316 has a vapor fraction of 55% and a temperature of -123°C. The mixed refrigerant for this third cooling loop 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.

[0065] Mixed refrigerant in line 316 is fully vaporized and warmed to 26°C in fourth heat exchanger 317 to provide refrigeration therein. Vaporized refrigerant in line 318 is compressed to 17.7 bar in first stage compressor 319, cooled to 36.5°C and partially liquefied in 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 bar. Refrigerant vapor in line 322 is compressed to a pressure of 47 bar 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. This mixed refrigerant is cooled in fourth heat exchanger 317 to provide cooled mixed refrigerant in line 329, which is further cooled in third heat exchanger 312 as earlier described.

[0066] 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 at least two heat exchange zones (310, 311 & 312) at respective temperature ranges to provide a liquefied product (13), wherein refrigeration for cooling the feed gas stream in said temperature ranges is provided by respective vaporizing refrigerants (117, 213 & 315) and the refrigerant (315) in the coldest temperature range is only partially vaporized in the coldest heat exchange zone (312) and recirculated in a recirculating refrigeration process that comprises further vaporizing the partially vaporized refrigerant (316) in a heat exchange zone (317) at temperatures above the highest temperature of the coldest heat exchange zone (312), compressing (319, 324) the further vaporized refrigerant (318) to yield a compressed refrigerant stream (328), and cooling the compressed refrigerant stream (328) to provide the coldest refrigerant (315), characterized in that the entire said compressed refrigerant stream (328) is cooled by (i) optionally cooling compressed refrigerant stream (328; 351) in a heat exchange zone (353) preceding the coldest heat exchange zone (312) by indirect heat exchange (352) with the respective vaporizing refrigerant (117); (ii) indirect heat exchange (317) of the optionally cooled stream (328; 354) with the further vaporizing refrigerant (316) to provide a cooled refrigerant stream (329), and (iii) further cooling the cooled refrigerant (329) stream to provide the coldest refrigerant (315).

2. A method of Claim 1, wherein said recirculating refrigeration process is self-refrigerated except for any cooling by said optional cooling step (i)

3. A method of Claim 1 or Claim 2, wherein cooling of the compressed refrigerant stream (328) does not comprise step (i).

4. A method of Claim 1 or Claim 2, wherein cooling of the compressed refrigerant stream (328; 351) comprises step (i).

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

6. A method of any one of the preceding claims, wherein the coldest refrigerant (i.e. the refrigerant in the coldest temperature range) (315) is a multi-component mixture comprising nitrogen, *i*-pentane and *n*-pentane with the molar ratio of *i*-pentane to *n*-pentane in the coldest refrigerant being greater than one, said *i*-pentane and *n*-pentane being obtained from the feed gas stream (1) and said molar ratio in the coldest refrigerant (315) is greater than the molar ratio of *i*-pentane to *n*-pentane in the feed gas stream (1).

7. A method of any one of Claims 1 to 5, wherein the coldest refrigerant (i.e. the refrigerant in the coldest temperature range) (315) is a multi-component mixture comprising nitrogen, *i*-pentane and one or more hydrocarbons having four carbon atoms, said *i*-pentane and one or more hydrocarbons are obtained from the feed gas stream (1), and the molar ratio of *i*-pentane to the one or more hydrocarbons having four carbon atoms in the coldest refrigerant (315) is greater than the molar ratio of *i*-pentane to one or more hydrocarbons having four carbon atoms in the feed gas stream (1).

8. A method of Claim 6 or Claim 7, wherein the coldest refrigerant (315) comprises (in mole %) 5-15% nitrogen, 30-60% methane, 10-30% ethane, 0-10% propane, and 5-15% *i*-pentane.

9. A method of any one of the preceding claims, wherein the further cooling of the cooled refrigerant stream (329) is effected by indirect heat exchange with the coldest refrigerant (315) vaporizing in the coldest heat exchange zone (312).

10. A method of any one of the preceding claims, wherein, prior to vaporization to cool the compressed refrigerant stream (328; 339), the partially vaporized refrigerant (316) is combined with a cooled reduced-pressure liquid refrigerant (345) to provide a combined two-phase refrigerant (347) that is vaporized to cool the compressed refrigerant stream (328; 339), the compressed refrigerant vapor (330) is cooled (332) to provide a partially-condensed refrigerant, the partially-condensed refrigerant is separated (333) into a refrigerant vapor stream (334) and a refrigerant liquid stream (335), the refrigerant vapor stream (334) is compressed (336) and cooled (337) to form a partially-

condensed stream and the partly-condensed stream is separated (338) into the compressed refrigerant vapor (328; 339) and a liquid refrigerant (340), the pressure of the liquid refrigerant is reduced (341) to provide a reduced-pressure liquid refrigerant (342), the reduced-pressure liquid refrigerant (342) is combined with the refrigerant liquid stream (335) to provide a combined refrigerant liquid (343), the combined refrigerant liquid stream (343) is subcooled by indirect heat exchange (344) with the combined two-phase refrigerant (347) to provide the cooled reduced-pressure liquid refrigerant (345) for combining with the partially vaporized refrigerant (316).

11. A system for liquefying a gas stream (1) by a method of Claim 1, which system comprises:

at least two heat exchange zones (310, 311 & 312) for cooling the gas stream (1) successively through respective temperature ranges to provide a liquefied product (13) and

respective refrigeration systems for providing respective refrigerants in respective refrigerant lines (117, 213 & 315) to the heat exchange zones (310, 311 & 312), the coldest temperature heat exchange zone (312) only partially vaporizing the respective (i.e. coldest) refrigerant

the refrigeration system providing the coldest refrigerant being a recirculating system comprising:

a further heat exchange zone (317) to further vaporize the resultant partially vaporized refrigerant at temperatures above the highest temperature of the coldest heat exchange zone (312),

compression means (319) for compressing the vaporized refrigerant to provide the compressed refrigerant stream (328),

piping means (318) to provide vaporized refrigerant from the further heat exchange zone (317) to said compression means (319),

piping means (328) to provide the compressed refrigerant to the further heat exchange zone (317),

piping means (329) for providing a cooled compressed refrigerant from the further heat exchange zone (317) to the coldest heat exchange zone (312), and

means to further cool (356) the cooled compressed refrigerant to provide a condensed refrigerant

characterized in that:

the piping means (328) providing the compressed refrigerant to the further heat exchange zone (317) conveys the entire compressed refrigerant stream (328) and optionally passes through a heat exchange zone (353) preceding the coldest heat exchange zone (312) to cool the compressed refrigerant by indirect heat exchange (352) with the respective vaporizing refrigerant (117.

12. A system of Claim 11, wherein said recirculating refrigeration system providing the coldest refrigerant process is self-refrigerated except for any cooling provided by said option of cooling in the preceding heat exchange zone (353).

13. A system of Claim 11 or Claim 12, wherein:

the means to further cool (356) the cooled compressed refrigerant to provide a condensed refrigerant comprises the coldest heat exchange zone (312) and

the system further comprises pressure reduction means (314) to reduce the pressure of the condensed refrigerant to provide the refrigerant to the refrigerant line (315) for the coldest heat exchange zone (312).

14. A system of Claim 13, wherein the further heat exchange zone (317; 344) includes means for subcooling a refrigerant liquid to provide a subcooled refrigerant liquid and the coldest refrigeration system comprises pressure reduction means (346) for reducing the pressure of the subcooled refrigerant liquid to provide a reduced-pressure refrigerant, and piping means (347) for combining the reduced-pressure refrigerant with the partially vaporized refrigerant from the coldest heat exchange zone (312) to provide a combined vaporizing refrigerant stream to the further heat zone (317; 344), wherein the combined vaporizing refrigerant stream vaporizes to provide the vaporized refrigerant feed to the compression means (319).

15. A system of Claim 14, wherein the compression means for compressing the vaporized refrigerant from the further heat exchange zone (344) comprises:

a first stage compressor (331),

an intercooler (332) to cool and partially condense the resultant first compressed refrigerant stream to yield a partially condensed first compressed refrigerant stream,

a first separator (333) to separate the partially condensed first compressed refrigerant stream into a first vapor refrigerant stream and a first liquid refrigerant stream,

a second stage compressor (336) to compress the vapor refrigerant stream to provide a compressed vapor refrigerant stream,

an aftercooler (337) to cool the compressed vapor refrigerant stream to provide a cooled two-phase refrigerant stream,

a second separator (338) to provide a second liquid refrigerant stream and the compressed refrigerant to the piping means (328) for feed to the further heat exchange zone (317),

pressure reduction means (341) to reduce the pressure of the second liquid refrigerant stream to provide a reduced-pressure second liquid refrigerant stream, and

piping means (335, 342, 343) to combine the reduced-pressure second liquid refrigerant stream and the first liquid refrigerant stream to provide the refrigerant liquid to the further heat exchange zone (344).

16. A system of Claim 11 for liquefying a gas stream (1) by a method of Claim 4, wherein the coldest refrigeration system comprises:

piping means (348) to provide vaporized refrigerant from the further heat exchange zone (317; 355) to compression means (349) for compressing a vaporized refrigerant to provide a compressed refrigerant,

cooling means (352) in a heat exchange zone (353) preceding the coldest heat exchange zone (312) for cooling the compressed refrigerant by indirect heat exchange with the respective refrigerant vaporizing in said heat exchange zone (353) to provide a cooled compressed refrigerant,

piping mean to provide the cooled compressed refrigerant to the further heat exchange zone (317; 355) to further cool the cooled compressed refrigerant by indirect heat exchange with the vaporizing refrigerant from the coldest heat exchange zone (312) to provide the vaporized third refrigerant and a further cooled compressed refrigerant,

means to further cool (356) the cooled compressed refrigerant in the coldest heat exchange zone (312) to provide a condensed refrigerant, and

pressure reduction means (314) to reduce the pressure of the condensed refrigerant to provide the refrigerant to the refrigerant line (315) for the coldest heat exchange zone (312).