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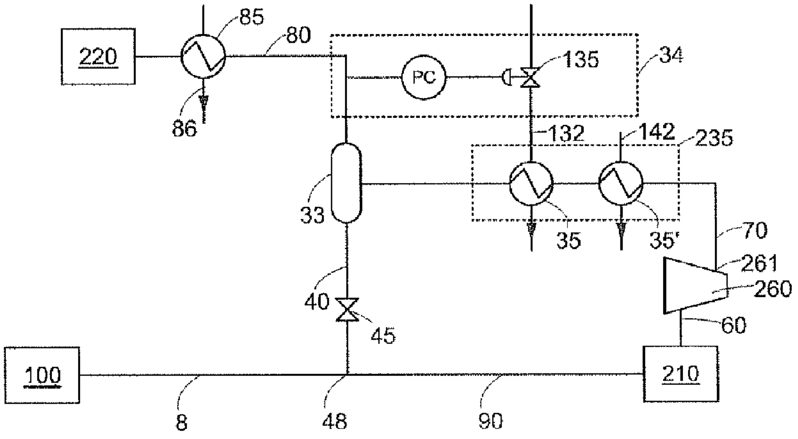
(72) **Inventeurs/Inventors:**
HARTENHOF, MICHA, NL;
SANTOS, ALEXANDRE M.C.R., MY

(73) **Propriétaire/Owner:**
SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V., NL

(74) **Agent:** NORTON ROSE FULBRIGHT CANADA
LLP/S.E.N.C.R.L., S.R.L.

(54) **Titre : PROCEDE ET APPAREIL PERMETTANT D'ELIMINER DE L'AZOTE D'UNE COMPOSITION D'HYDROCARBURE CRYOGENIQUE**
(54) **Title: METHOD AND APPARATUS FOR REMOVING NITROGEN FROM A CRYOGENIC HYDROCARBON COMPOSITION**



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Nitrogen is removed from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase. A by-product vapour from the cryogenic hydrocarbon composition, at a low pressure of between and 2 bar absolute, is compressed to a separation pressure in the range of between 2 and 15 bar absolute. The such compressed vapour is partially liquefied by heat exchanging the compressed vapour against an auxiliary refrigerant stream and thereby passing heat from the compressed vapour to the auxiliary refrigerant stream at a cooling duty. The condensed fraction of the partially liquefied compressed vapour is depressurized and at least a portion of it is reinjected into the cryogenic hydrocarbon composition. An off gas consisting of a, non condensed, vapour fraction of the partially liquefied compressed vapour is discharged from the first gas/liquid separator. The cooling duty is adjusted to regulate a heating value of the vapour fraction being discharged.

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(71) **Applicant** *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(71) **Applicant** *(for US only)*: **SHELL OIL COMPANY** [US/US]; PO Box 2463, One Shell Plaza, Houston, Texas 77252-2463 (US).

(72) **Inventors**: **HARTENHOF, Micha**; Kesslerpark 1, NL-2288 GS Rijswijk (NL). **SANTOS, Alexandre M.C.R.**; Changkat Semantan, Damansara Heights, Kuala Lumpur, 50490 (MY).

(74) **Agent**: **MATTHEZING, Robert Maarten**; PO Box 384, NL-2501 CJ The Hague (NL).

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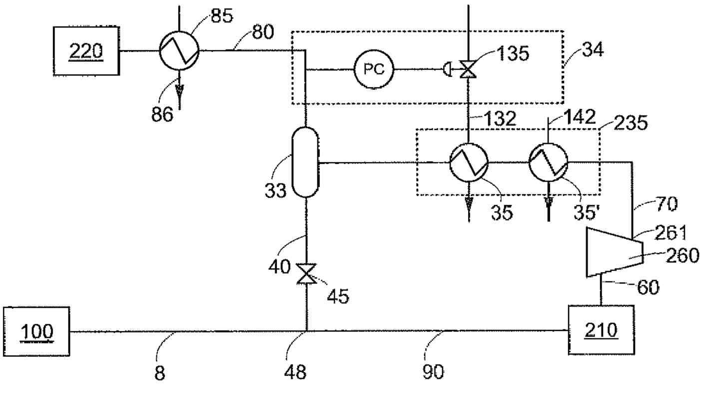

FIG. 1

(57) **Abstract**: Nitrogen is removed from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase. A by-product vapour from the cryogenic hydrocarbon composition, at a low pressure of between and 2 bar absolute, is compressed to a separation pressure in the range of between 2 and 15 bar absolute. The such compressed vapour is partially liquefied by heat exchanging the compressed vapour against an auxiliary refrigerant stream and thereby passing heat from the compressed vapour to the auxiliary refrigerant stream at a cooling duty. The condensed fraction of the partially liquefied compressed vapour is depressurized and at least a portion of it is reinjected into the cryogenic hydrocarbon composition. An off gas consisting of a, non condensed, vapour fraction of the partially liquefied compressed vapour is discharged from the first gas/liquid separator. The cooling duty is adjusted to regulate a heating value of the vapour fraction being discharged.

WO 2013/076185 A3

METHOD AND APPARATUS FOR REMOVING NITROGEN FROM A CRYOGENIC HYDROCARBON COMPOSITION

The present invention relates to a method and apparatus for removing nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase.

Liquefied natural gas (LNG) forms an economically important example of such a cryogenic hydrocarbon composition. Natural gas is a useful fuel source, as well as a source of various hydrocarbon compounds. It is often desirable to liquefy natural gas in a liquefied natural gas plant at or near the source of a natural gas stream for a number of reasons. As an example, natural gas can be stored and transported over long distances more readily as a liquid than in gaseous form because it occupies a smaller volume and does not need to be stored at high pressure.

WO 2006/120127 describes an LNG separation process and installation. Liquefied natural gas in liquid form is sent to a separation unit, wherein a stream of LNG purified of nitrogen, and a nitrogen-enriched vapour are produced. The separation unit employs two columns. The nitrogen-enriched vapour is recondensed in an overhead condenser of one of the columns, by means of a refrigerant fluid, the nitrogen content of which is greater than 80 mol%. Herewith the production of LNG is increased, since the methane molecules, otherwise lost with the nitrogen-enriched vapour, may now be recovered as LNG. The boil-off from storage may also be treated and recondensed. The nitrogen contained in the natural gas can be utilized at commercial purity.

A drawback of this LNG separation process is that the nitrogen-enriched stream is not suitable as a fuel stream.

The present invention provides a method of removing nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase, the method comprising:

- providing a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase at an initial pressure of between 1 and 2 bar absolute;
- collecting a by-product vapour from the cryogenic hydrocarbon composition;
- compressing said by-product vapour to a treatment pressure in the range of between 2 and 15 bar absolute, thereby obtaining a compressed vapour;
- forming a partially condensed intermediate stream from the compressed vapour comprising a condensed fraction and a vapour fraction, said forming comprising partially condensing the compressed vapour by heat exchanging the compressed vapour against an auxiliary refrigerant stream and thereby passing heat from the compressed vapour to the auxiliary refrigerant stream at a cooling duty;
- separating the condensed fraction from the vapour fraction in a first gas/liquid separator, at a separation pressure of between 2 and 15 bar absolute;
- discharging the vapour fraction from the first gas/liquid separator as off gas, said vapour fraction having a heating value;
- discharging the condensed fraction of the first gas/liquid separator;

- depressurizing the condensed fraction to a pressure not lower than the initial pressure, thereby forming a depressurized recycle portion;
- injecting the depressurized recycle portion into the cryogenic hydrocarbon composition;
- adjusting the cooling duty to regulate the heating value of the vapour fraction being discharged from the first gas/liquid separator.

In another aspect, the present invention provides an apparatus for removing nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase, the apparatus comprising:

- a holder for a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase at an initial pressure;
- a by-product vapour line fluidly connected to the holder and arranged to collect a by-product vapour from the holder;
- a by-product compressor arranged in the by-product vapour line arranged to compress at least said by-product vapour to a treatment pressure that exceeds the initial pressure to provide a compressed vapour at a compressor discharge outlet of the by-product compressor;
- at least one condensing heat exchanger in fluid communication with the compressor discharge outlet and arranged to receive the compressed vapour and to form partially condensed intermediate stream out of the compressed vapour, the partially condensed intermediate stream comprising a condensed fraction and a vapour fraction, and said condensing heat exchanger furthermore arranged to bring the compressed vapour in a heat exchanging contact with an auxiliary refrigerant stream

whereby during operation heat passes from the compressed vapour to the auxiliary refrigerant stream at a cooling duty;

- a first gas/liquid separator arranged to receive the partially condensed intermediate stream and to separate the condensed fraction from the vapour fraction at a separation pressure;
- a vapour fraction discharge line fluidly connected to the first gas/liquid separator, arranged to convey the vapour fraction away from the first gas/liquid separator;
- a condensed fraction discharge line arranged to convey the condensed fraction away from the first gas/liquid separator, said condensed fraction discharge line on an upstream end thereof fluidly connected to the first gas/liquid separator and on a downstream end thereof in fluid communication with an injection point in confluence with the cryogenic hydrocarbon composition;
- a depressurizing system disposed in the condensed fraction discharge line, arranged to depressurize the condensed fraction to a pressure not lower than the initial pressure, thereby forming a depressurized recycle portion;
- a cooling duty controller arranged to adjust the cooling duty to regulate a heating value of the vapour fraction being discharged from the first gas/liquid separator.

The invention will be further illustrated hereinafter, using examples and with reference to the drawing in which;

Fig. 1 schematically represents a process flow scheme representing a method and apparatus according to an embodiment of the invention;

Fig. 2 schematically represents a process flow scheme representing a method and apparatus according to another embodiment of the invention;

Fig. 3 schematically represents a process flow scheme including a method and apparatus according to still another embodiment of the invention; and

Fig. 4 schematically represents a process flow scheme including a method and apparatus according to still another embodiment of the invention.

In these figures, same reference numbers will be used to refer to same or similar parts. Furthermore, a single reference number will be used to identify a conduit or line as well as the stream conveyed by that line.

The present description concerns removal of nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase. A by-product vapour from the cryogenic hydrocarbon composition, at a low pressure of between 1 and 2 bar absolute, is compressed to a separation pressure in the range of between 2 and 15 bar absolute. The such compressed vapour is partially liquefied by heat exchanging the compressed vapour against an auxiliary refrigerant stream and thereby passing heat from the compressed vapour to the auxiliary refrigerant stream at a cooling duty. The condensed fraction of the partially liquefied compressed vapour is depressurized and at least a portion of it is reinjected into the cryogenic hydrocarbon composition. An off gas consisting of a, non condensed, vapour fraction of the partially liquefied compressed vapour is discharged from the first gas/liquid separator. The cooling duty is adjusted to control a heating value of the vapour fraction being discharged.

By adjusting the cooling duty at which heat is passed from the compressed vapour to the auxiliary refrigerant stream, the relative amount of methane in the off gas can be regulated. As a result, the heating value of the discharged vapour fraction can be regulated to match with a specific demand of heating power. This renders the off gas suitable for use as fuel gas stream, even in circumstances where the demand for heating value is variable.

Preferably the off gas is consumed at a fuel gas pressure not higher than the separation pressure. Herewith the need of a dedicated fuel gas compressor can be avoided.

In the context of the present description, cooling duty reflects the rate at which heat is exchanged in the condensing heat exchanger, which can be expressed in units of power (e.g. Watt or MWatt). The cooling duty is related to the flow rate of the auxiliary refrigerant being subjected to the heat exchanging against the compressed vapour.

The heating value being regulated may be selected in accordance with the appropriate circumstances of the intended use of the off gas as fuel gas. The heating value may be determined in accordance with DIN 51857 standards. For many applications, the heating value being regulated may be proportional to the lower heating value (LHV; sometimes referred to as net calorific value), which may be defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C. This assumes the latent heat of vaporization of water in the reaction products is not recovered.

However, for the purpose of regulating the heating value in the context of the present disclosure, the actual heating value of the vapour fraction being discharged does not need to be determined on an absolute basis. Generally it is sufficient to regulate the heating value relative to an actual demand for heating power, with the aim to minimize any shortage and excess of heating power being delivered.

Preferably, the cooling duty is automatically adjusted in response to a signal that is causally related to the heating value being regulated.

It is anticipated that the presently proposed methods and apparatus are most beneficial when the raw liquefied product, or the cryogenic hydrocarbon composition, contains from 0.5 mol% up to 1.8 mol% of nitrogen. Existing alternative approaches may work adequately when the nitrogen content is outside of this range. For instance, for higher nitrogen contents, a nitrogen stripper column may be employed.

The proposed method and apparatus allow for re-condensation of vaporous methane that has previously formed part of the raw liquefied product, to the extent that it is in excess of a target amount of methane in the discharged vapour fraction, by adding any such vaporous methane containing stream to the vapour or compressed stream. Once forming part of the compressed vapour, the vaporous methane can find its way to the heat exchanging with the auxiliary refrigerant by which it is selectively condensed out of the compressed vapour, while allowing the majority of the nitrogen to be discharged with the off gas. Herewith it becomes possible to remove sufficient nitrogen from the cryogenic hydrocarbon composition to produce a liquid hydrocarbon product stream within a desired maximum specification of nitrogen content, while as the same time not producing more heating capacity in the off gas than needed.

Vaporous methane that has previously formed part of the raw liquefied product can be formed in an LNG liquefaction plant due to various reasons. During normal operation of a natural gas liquefaction facility, methane containing by-product vapour is formed from the (raw) liquefied product in the form of:

- flash vapour resulting from flashing of the raw liquefied product during depressurizing; and
- boil-off gas resulting from thermal evaporation caused by heat added to the liquefied product, for instance in the form of heat leakage into storage tanks, LNG piping, and heat input from plant LNG pumps. During this mode of operation, known as holding mode operation, the storage tanks are being filled with the liquefied hydrocarbon product as it comes out of the plant without any transporter loading operations taking place at the same time. When in holding mode, the methane-containing by-product vapours are generated on the plant side of the storage tanks.

The operation mode of an LNG plant while there are ongoing transporter loading operations (typically ship loading operations) is known as loading mode operation. During loading mode operation, boil-off gas is additionally produced on the ship side of the storage tanks, for instance due to initial chilling of the ship tanks; vapour displacement from the ship tanks; heat leakage through piping and vessels connecting the storage tanks and the ships, and heat input from LNG loading pumps.

The proposed solution may facilitate the handling of these by-product vapours both during holding mode and loading mode operations. It combines the removal of nitrogen from the cryogenic hydrocarbon composition with re-condensation of excess vaporous methane. This forms an elegant solution in situations where little plant fuel is demanded, such as could be the case in an electrically driven plant using electric power from an external power grid.

The proposed method and apparatus are specifically suitable for application in combination with a hydrocarbon liquefaction system, such as a natural gas liquefaction system, in order to remove nitrogen from a raw liquefied product. It has been found that even when the raw liquefied product - or the cryogenic hydrocarbon composition - contains a fairly high amount of from 1.0 mol% (or from about 1.0 mol%) up to 1.8 mol% (or up to about 1.8 mol%) of nitrogen, the resulting liquid hydrocarbon product can meet a nitrogen content within a specification of between from 0.5 to 1 mol% nitrogen. The remainder of the nitrogen is discharged as part of the vapour fraction in the off gas, together with a controlled amount of methane.

Notwithstanding, the proposed solution is also beneficial for cryogenic hydrocarbon compositions containing less than 1.0 mol% of nitrogen, because the proposed solution can be arranged to accommodate boil-off gas while maintaining control over the amount of methane that is shedded as part of the vapour fraction in the off gas with the aim to minimize any shortage and excess of heating power being delivered compared to the actual demand of heating power.

It is noted that WO 2011/009832 describes a method by which nitrogen can be separated from a multi-phase hydrocarbon stream, wherein a vapour is compressed and returned to a first gas/liquid separator in vapour form as a stripping vapour stream. The first gas/liquid separator of WO 2011/009832 is essentially a column, because it uses a contacting zone comprising contact enhancing means.

In the present invention, the vapour stream is partly condensed before feeding it to the first gas/liquid separator. The vapour fraction is not employed as stripping vapour, but merely separated from the condensed fraction. Characteristic is that the temperature of the vapour fraction being discharged from the first gas/liquid separator is essentially the same (for instance not differing by more than 2°C or preferably by more than 1°C) as the temperature of the condensed fraction being discharged from the first gas/liquid separator. The first gas/liquid separator may represent essentially a single equilibrium stage wherein vapour and liquid inside the gas/liquid separator are in thermodynamic equilibrium. An advantage of the presently proposed apparatus and methods is that first gas/liquid separator may consist of a drum that is free from any internals that form a vapour/liquid contacting section. This can be a simple phase separator vessel, arranged to separate an incoming vapour phase from an incoming liquid phase.

This makes it significantly cheaper and less complex to operate than for instance the line-up disclosed in WO 2006/120127, which employs two columns, or WO 2011/009832 which employs essentially one column.

Figure 1 illustrates an apparatus comprising an embodiment of the invention. A cryogenic feed line 8 is in fluid communication with a cryogenic storage tank 210, such that at least a part of a cryogenic hydrocarbon composition being conveyed in the cryogenic feed line 8 is transported into the cryogenic storage tank 210. In the embodiment of Figure 1, a liquid hydrocarbon product line 90 connects the cryogenic feed line 8 with the cryogenic storage tank 210.

Upstream of the cryogenic feed line 8, a liquefaction system 100 may be provided. The liquefaction system 100 functions as a source of a cryogenic hydrocarbon composition. Preferably, but not necessarily, any compressor forming part of the hydrocarbon liquefaction process in the liquefaction system, particularly any refrigerant compressor, is driven by one or more electric motors, without being mechanically driven by any steam- and/or gas turbine. Such compressor may be driven exclusively by one or more electric motors.

In the embodiment of Figure 1, the cryogenic storage tank 210 fulfils the function of a holder for the cryogenic hydrocarbon composition. The present invention is not limited to holders in the form of a cryogenic storage tank such as is exemplified in Figure 1, but works with any type of holder for the cryogenic hydrocarbon composition, including for instance a pipe, a phase separator, a cargo tank on a transporter, or various combinations. Figure 2, which will be described in more detail below, shows an example wherein the holder comprises a combination of a pipe, a phase separator and a cryogenic storage tank.

A by-product vapour line 60 is fluidly connected to the cryogenic storage tank 210. The by-product vapour line 60 is arranged to collect a by-product vapour from the holder. A by-product compressor 260 is arranged in the by-product vapour line 60, to compress the by-product vapour in the by-product vapour line 60. A compressed vapour discharge line 70 is fluidly connected with a compressor discharge outlet 261 of the by-product compressor 260. Suitably, the by-product compressor 260 is provided with anti-surge control and a recycle cooler which is used when the by-product compressor is on recycle and during start-up (not shown in the drawing).

A condensing heat exchanger train 235 comprising at least one condensing heat exchanger 35 is provided in the compressed vapour discharge line 70 in fluid communication with the compressor discharge outlet 261. The condensing heat exchanger train 235 may comprise at least one supplemental condensing heat exchanger 35′ in addition to the condensing heat exchanger 35, in which supplemental condensing heat exchanger 35′ the compressed vapour line 70 is configured in indirect heat exchanging relationship with a supplemental refrigerant line 142. The supplemental refrigerant line can be supplied with any selected supplemental refrigerating stream. Examples of such supplemental condensing heat exchangers 35′ will be described below. By operating such supplemental condensing heat exchanger 35′, the duty required from the auxiliary refrigerant stream 132 in the condensing heat exchanger 35 would be reduced.

The condensing heat exchanger train 235 is arranged to receive the compressed vapour from the compressor discharge outlet 261. Inside the condensing heat exchanger 35 the compressed vapour can pass in indirect heat exchange contact with an auxiliary refrigerant stream 132, whereby during operation heat passes from the compressed vapour to the auxiliary refrigerant stream 132 at a cooling duty. An auxiliary refrigerant stream flow control valve 135 is provided in the auxiliary refrigerant line 132.

A cooling duty controller 34 controls the cooling duty, being the rate at which heat passes from the compressed vapour to the auxiliary refrigerant stream, in response to an indicator of heating value of the off gas relative to a demand for heating power. In the embodiment as shown, the cooling duty controller 34 is embodied in the form of a pressure controller PC and the auxiliary refrigerant stream flow control valve 135, which are functionally coupled to each other.

A first gas/liquid separator 33 is arranged in a downstream end of the compressed vapour discharge line 70. A vapour fraction discharge line 80 is fluidly connected to the first gas/liquid separator 33, arranged to convey a vapour fraction that is discharged from the first gas/liquid separator 33 away from the first gas/liquid separator 33. The thus discharged vapour fraction forms an off gas.

A combustion device 220 is arranged at a downstream end of the vapour fraction discharge line 80, to receive at least a fuel portion of the vapour fraction in the vapour fraction discharge line 80. The combustion device may comprise multiple combustion units, and/or it may include for example one or more of a furnace, a boiler, an incinerator, a dual fuel diesel engine, or combinations thereof. A boiler and a duel fuel diesel engine may be coupled to an electric power generator.

An off gas cold recovery heat exchanger 85 may be provided in the vapour fraction discharge line 80, to preserve the cold vested in the vapour fraction 80 by heat exchanging against a cold recovery stream 86 prior to feeding the vapour fraction 80 to any combustion device.

Suitably, the off gas cold recovery heat exchanger 85 may form part of the condensing heat exchanger train 235 in the position of the supplemental condensing heat exchanger 35′, whereby the cold recovery stream 86 may comprise, or consist of, the compressed vapour in the compressed vapour discharge line 70 and whereby the vapour fraction 80 functions as the supplemental refrigeration stream 142. Preferably the off gas cold recovery heat exchanger 85 is configured in a part of the compressed vapour discharge line 70 where through the compressed vapour is passed from the compressor discharge outlet 261 to the condensing heat exchanger 35.

A condensed fraction discharge line 40 is, on an upstream end thereof, fluidly connected to the first gas/liquid separator 33 and arranged to convey a condensed fraction away from the first gas/liquid separator 33. On a downstream end thereof, the condensed fraction discharge line 40 is in fluid communication with an injection point 48 into cryogenic feed line 8. The injection point 48 is in confluence with the cryogenic hydrocarbon composition, and forms the connection between the cryogenic feed line 8 and the liquid hydrocarbon product line 90.

A depressurizing system 45 is disposed in the condensed fraction discharge line 40. The depressurizing system 45 may suitably be functionally coupled to a level controller cooperating with the first gas/liquid separator 33 to maintain the amount of the condensed fraction that is held up inside the first gas/liquid separator 33 constant.

Figure 2 presents an embodiment generally like Figure 1, wherein a second gas/liquid separator is provided between the cryogenic feed line 8 and the liquid hydrocarbon product line 90. The second gas/liquid separator usually provided in the form of an end flash separator 50. If the condensed fraction discharge line 40 discharges into the second gas/liquid separator, the second gas/liquid separator can replace the injection point 48 into cryogenic feed line 8. Alternatively, the injection point 48 (shown by a dotted line in Figure 2) in the cryogenic hydrocarbon composition line 8 is employed, whereby a combined stream 10 is first formed between the depressurized condensed fraction and the cryogenic hydrocarbon composition in the cryogenic hydrocarbon composition line 8. Thus, in such embodiments, in the order encountered starting from the cryogenic feed line 8, the cryogenic feed line 8 is in fluid communication with the cryogenic storage tank 210 via: the end flash separator 50 the liquid hydrocarbon product line 90 which is fluidly connected with a lower part of the end flash separator 50.

An optional cryogenic pump (not shown in Figure 2 but shown in Figure 3) may be present in the liquid hydrocarbon product line 90, to assist the transport of any liquid hydrocarbon product that is being discharged from the end flash separator to the cryogenic storage tank 210.

The liquefaction system 100 in the embodiment of Figure 2 is in fluid communication with the cryogenic feed line 8 via a main depressurizing system 5. The main depressurizing system 5 communicates with the liquefaction system 100 via a raw liquefied product line 1. The main depressurizing system 5 may comprise a dynamic unit, such as an expander turbine, a static unit, such as a Joule Thomson valve, or a combination thereof. Many arrangements are possible.

The by-product vapour line 60, as shown in the embodiment of Fig. 2, may be connected to the end flash separator 50 via a flash vapour line 64. Optionally (not shown in Fig. 3) the flash vapour line 64 configured in indirect heat exchanging arrangement with the compressed vapour line 70, suitably using one of the supplemental condensing heat exchangers 35′ as described above.

In a typical LNG plant the generation of boil-gas can exceed the flow rate of flash vapour by multiple times, particularly during operating the plant in so-called loading mode, and hence it is an important benefit to not only re-condense the flash vapour but to re-condense boil-off gas as well if there is not enough on-site demand for heating power to use all of the methane contained in the boil-off gas. Therefore it is preferred that the by-product vapour line 60 is also in fluid combination with the cryogenic storage tank 210, for instance via an optional boil-off gas supply line 230. An advantage of the latter connection is that it allows for re-condensing of at least part of the boil-off gas from the cryogenic storage tank 210 by means of the condensing heat exchanger train 235, in addition to re-condensing flash vapour being discharged from the end flash separator 50. In this embodiment, the holder for the cryogenic hydrocarbon composition includes both the end flash separator 50 and the cryogenic storage tank 210. If the liquid hydrocarbon product line 90 is relatively long, is may act as an additional source of boil-off gas and as such also form part of the holder for the cryogenic hydrocarbon composition.

The remaining components in the embodiment of Figure 2 correspond to those already described above with reference to Figure 1.

The liquefaction system 100 in the present specification has so far been depicted very schematically. It can represent any suitable hydrocarbon liquefaction system and/or process, in particular any natural gas liquefaction process producing liquefied natural gas, and the invention is not limited by the specific choice of liquefaction system. Examples of suitable liquefaction systems employ single refrigerant cycle processes (usually single mixed refrigerant - SMR - processes, such as PRICO described in the paper "LNG Production on floating platforms" by K R Johnsen and P Christiansen, presented at Gastech 1998 (Dubai), but also possible is a single component refrigerant such as for instance the BHP-cLNG process also described in the afore-mentioned paper by Johnsen and Christiansen); double refrigerant cycle processes (for instance the much applied Propane-Mixed-Refrigerant process, often abbreviated C3MR, such as described in for instance US Patent 4,404,008, or for instance double mixed refrigerant - DMR - processes of which an example is described in US Patent 6,658,891, or for instance two-cycle processes wherein each refrigerant cycle contains a single component refrigerant); and processes based on three or more compressor trains for three or more refrigeration cycles of which an example is described in US Patent 7,114,351.

Other examples of suitable liquefaction systems are described in: US Patent 5,832,745 (Shell SMR); US Patent 6,295,833; US Patent 5,657,643 (both are variants of Black and Veatch SMR); US Pat. 6,370,910 (Shell DMR).

Another suitable example of DMR is the so-called Axens LIQUEFIN process, such as described in for instance the paper entitled “LIQUEFIN: AN INNOVATIVE PROCESS TO REDUCE LNG COSTS” by P-Y Martin *et al*, presented at the 22nd World Gas Conference in Tokyo, Japan (2003). Other suitable three-cycle processes include for example US Pat. 6,962,060; WO 2008/020044; US Pat. 7,127,914; DE3521060A1; US Pat. 5,669,234 (commercially known as optimized cascade process); US Pat. 6,253,574 (commercially known as mixed fluid cascade process); US Pat. 6,308,531; US application publication 2008/0141711; Mark J. Roberts *et al* “Large capacity single train AP-X(TM) Hybrid LNG Process”, Gastech 2002, Doha, Qatar (13-16 October 2002). These suggestions are provided to demonstrate wide applicability of the invention, and are not intended to be an exclusive and/or exhaustive list of possibilities. Not all examples listed above employ electric motors as refrigerant compressor drivers. It will be clear that any drivers other than electric motors can be replaced for an electric motor to enjoy the most benefit of the present invention.

An example, wherein in the liquefaction system 100 is based on, for instance C3MR or Shell DMR, is briefly illustrated in Figure 3. It employs a cryogenic heat exchanger 180, in this case in the form of a coil wound heat exchanger comprising lower and upper hydrocarbon product tube bundles (181 and 182, respectively), lower and upper LMR tube bundles (183 and 184, respectively) and an HMR tube bundle 185.

The lower and upper hydrocarbon product tube bundles 181 and 182 fluidly connect the raw liquefied product line 1 with a hydrocarbon feed line 110. At least one refrigerated hydrocarbon pre-cooling heat exchanger 115 may be provided in the hydrocarbon feed line 110 upstream of the cryogenic heat exchanger 180.

A main refrigerant, in the form of a mixed refrigerant, is provided in a main refrigerant circuit 101. The main refrigerant circuit 101 comprises a spent refrigerant line 150, connecting the cryogenic heat exchanger 180 (in this case a shell side 186 of the cryogenic heat exchanger 180) with a main suction end of a main refrigerant compressor 160, and a compressed refrigerant line 120 connecting a main refrigerant compressor 160 discharge outlet with an MR separator 128. One or more heat exchangers are provided in the compressed refrigerant line 120, including in the present example at least one ambient heat exchanger 124 and at least one refrigerated main refrigerant pre-cooling heat exchanger 125. The MR separator 128 is in fluid connection with the lower LMR tube bundle 183 via a light refrigerant fraction line 121, and with the HMR tube bundle via a heavy refrigerant fraction line 122.

The at least one refrigerated hydrocarbon pre-cooling heat exchanger 115 and the at least one refrigerated main refrigerant pre-cooling heat exchanger 125 are refrigerated by a pre-cooling refrigerant (via lines 127 and 126, respectively). The same pre-cooling refrigerant may be shared from the same pre-cooling refrigerant cycle. Moreover, the at least one refrigerated hydrocarbon pre-cooling heat exchanger 115 and the at least one refrigerated main refrigerant pre-cooling heat exchanger 125 may be combined into one pre-cooling heat exchanger unit (not shown). Reference is made to US Pat. 6,370,910 as a non-limiting example.

At a transition point between the upper (182, 184) and lower (181, 183) tube bundles, the HMR tube bundle

185 is in fluid connection with an HMR line 141. The HMR line 141 is in fluid communication with the shell side 186 of the cryogenic heat exchanger 180 via a first HMR return line 143, in which an HMR control valve 144 is configured. Via the said shell side 186, and in heat exchanging arrangement with each of one of the lower hydrocarbon product tube bundle 181 and the lower LMR tube bundle 183 and the HMR tube bundle 185, first HRM return line 143 is fluidly connected to the spent refrigerant line 150.

Above the upper tube bundles 182 and 184, near the top of the cryogenic heat exchanger 180, the LMR tube bundle 184 is in fluid connection with an LMR line 131. A first LMR return line 133 establishes fluid communication between the LMR line 131 and the shell side 186 of the cryogenic heat exchanger 180. An LMR control valve 134 is configured in the first LMR return line 133. The first LMR return line 133 is in fluid communication with the spent refrigerant line 150, via said shell side 186 and in heat exchanging arrangement with each of one of the upper and lower hydrocarbon product tube bundles 182 and 181, respectively, and each one of the LMR tube bundles 183 and 184, and the HMR tube bundle 185.

The line-up around the first gas/liquid separator shares many elements as explained above with reference to Figure 1 and/or Figure 2, and those elements will not be explained in full detail again. Figure 3 reveals one possible source of the auxiliary refrigerant, which can also be applied on the embodiments of Figures 1 and 2: the LMR line 131 is split into the auxiliary refrigerant line 132 and the first LMR return line 133. A second LMR return line 138 on an upstream end thereof fluidly connects with the auxiliary refrigerant line 132 via the condensing heat exchanger 35, and on a downstream end the second LMR return line 138 ultimately connects with the spent refrigerant line 150, suitably via the first HMR return line 143.

As different example of the condensing heat exchanger train 235, the supplemental condensing heat exchanger 35′ (depicted in Figure 1) is provided in the form of a slip-stream heat exchanger 37 as shown in Figure 3. The supplemental refrigerant line 142 (described above with reference to Figure 1) is in this case connected to one of the refrigerant circuits (e.g. the main refrigerant circuit 101) of the liquefaction system 100 to receive a split stream from the liquefaction system 100. In the example as shown in Figure 3, the HMR line 141 is split into the supplemental refrigerant line 142 and the first HMR return line 143. A second HMR return line 148 (on an upstream end thereof) fluidly connects with the supplemental refrigerant line 142 via the slip-stream heat exchanger 37, and on a downstream end this second HMR return line 148 connects with the spent refrigerant line 150. Alternatively, the supplemental refrigerant line 142 may for instance be sourced with a split stream from a pre-cooling refrigerant circuit from the liquefaction system 100.

In the embodiment of Figure 3, the off gas cold recovery heat exchanger 85 is configured in the boil-off gas supply line 230. Heat that may have been picked up by the boil-off gas on its route from the cryogenic storage tank 210 to the by-product compressor 260 may be extracted in part or fully by the vapour fraction 80, before feeding the boil-off gas from the boil-off gas supply line 230 into the by-product compressor 260 and/or into the by-product vapour line 60. This may be particularly useful if the cryogenic storage tank 210 is located at a significant distance D, for instance more than 1 km (for example D = about 4 km), from the by-product compressor 260. A conveyor compressor 270 may also be configured in the boil-off gas supply line 230, at the site of the cryogenic storage tank 210 (for instance, within a distance of 100 m from the cryogenic storage tank 210). In addition to heat leakage into the boil-off gas supply line 230, enthalpy is also added to the boil-off gas by such a conveyor compressor 270.

In alternative embodiments, the cold recovery stream may 86 comprise, or consist of, a side stream sourced from the hydrocarbon feed stream in the hydrocarbon feed line 110 of the liquefaction system 100. The resulting cooled side stream may for instance be combined with the cryogenic hydrocarbon composition in the cryogenic feed line 8. In such embodiments, the cold recovery heat exchanging in the off gas cold recovery heat exchanger 85 supplements the production rate of the cryogenic hydrocarbon composition.

Alternatively, the off gas cold recovery heat exchanger 85 may be configured in a part of the compressed vapour discharge line 70 where through the compressed vapour is passed from the compressor discharge outlet 261 to the condensing heat exchanger 35.

The method of removing nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase may be operated as follows.

A cryogenic hydrocarbon composition 8 comprising a nitrogen- and methane-containing liquid phase is provided at an initial pressure of between 1 and 2 bar absolute, and preferably a temperature lower than -130 °C.

The cryogenic hydrocarbon composition 8 may be obtained from natural gas or petroleum reservoirs or coal beds. As an alternative the cryogenic hydrocarbon composition 8 may also be obtained from another source, including as an example a synthetic source such as a Fischer-Tropsch process. Preferably the cryogenic hydrocarbon composition 8 comprises at least 50 mol% methane, more preferably at least 80 mol% methane.

In typical embodiments, the temperature of lower than -130 °C can be achieved by passing a hydrocarbon feed stream 110 through the liquefaction system 100. In such a liquefaction system 100, the hydrocarbon feed stream 110 comprising a hydrocarbon-containing feed vapour may be heat exchanged, for example in the cryogenic heat exchanger 180, against a main refrigerant stream, thereby liquefying the feed vapour of the feed stream to provide a raw liquefied stream within the raw liquefied product line 1. The desired cryogenic hydrocarbon composition 8 may then be obtained from the raw liquefied stream 1.

The main refrigerant stream may be generated by cycling the main refrigerant in the main refrigerant circuit 101, whereby spent refrigerant 150 is compressed in the main refrigerant compressor 160 to form a compressed refrigerant 120 out of the spent refrigerant 150. Heat is removed from the compressed refrigerant discharged from the main refrigerant compressor 160 is via the one or more heat exchangers that are provided in the compressed refrigerant line 120. This results in a partially condensed compressed refrigerant, which is phase separated in the MR separator 128 into a light refrigerant fraction 121 consisting of the vaporous constituents of the partially condensed compressed refrigerant, and a heavy refrigerant fraction 122 consisting of the liquid constituents of the partially condensed compressed refrigerant.

The light refrigerant fraction 121 is passed via successively the lower LMR bundle 183 and the upper LMR bundle 184 through the cryogenic heat exchanger 180, while the heavy refrigerant fraction 122 is passed via the HMR bundle 185 through the cryogenic heat exchanger 180 to the transition point. While passing through these respective tube bundles, the respective light- and heavy refrigerant fractions are cooled against the light and heavy refrigerant fractions that are evaporating in the shell side 186 again producing spent refrigerant 150 which completes the cycle. Simultaneously, the hydrocarbon feed stream 110 passes through the cryogenic heat exchanger 180 via successively the lower hydrocarbon bundle 181 and the upper hydrocarbon bundle 182 and is being liquefied and sub-cooled against the same evaporating light and heavy refrigerant fractions.

Depending on the source, the hydrocarbon feed stream 110 may contain varying amounts of components other than methane and nitrogen, including one or more non-hydrocarbon components other than water, such as CO_2, Hg, H_2S and other sulphur compounds; and one or more hydrocarbons heavier than methane such as in particular ethane, propane and butanes, and, possibly lesser amounts of pentanes and aromatic hydrocarbons. Hydrocarbons with a molecular mass of at least that of propane may herein be referred to as C_3+ hydrocarbons, and hydrocarbons with a molecular mass of at least that of ethane may herein be referred to as C_2+ hydrocarbons.

If desired, the hydrocarbon feed stream 110 may have been pre-treated to reduce and/or remove one or more of undesired components such as CO_2 and H_2S, or have undergone other steps such as pre-pressurizing or the like. Such steps are well known to the person skilled in the art, and their mechanisms are not further discussed here. The composition of the hydrocarbon feed stream 110 thus varies depending upon the type and location of the gas and the applied pre-treatment(s).

The raw liquefied stream 1 may comprise between from 0.5 mol% to 1.8 mol% nitrogen and be at a raw temperature of between from -165 °C to -120 °C and, if the main depressurizing system 5 is provided, at a liquefaction pressure of between from 15 bara to 120 bara. If such the main depressurizing system 5 is not provided, such as for example in the embodiment of Figure 1, the liquefaction pressure is preferably in the range of from 1 to 15 bara, preferably at the initial pressure of in the range of from 1 to 2 bara to directly deliver the cryogenic hydrocarbon composition 8 in the form of the raw liquefied stream. Otherwise, the cryogenic hydrocarbon composition 8 may be obtained from the raw liquefied stream 1 by main depressurizing the raw liquefied stream 1 from the liquefaction pressure to the initial pressure. Flash vapour is usually generated during such depressurizing.

In many cases, the raw temperature may be between from -155 °C to -140 °C. Within this more narrow range the cooling duty needed in the liquefaction system 100 is lower than when lower temperatures are desired, while the amount of sub-cooling at the pressure of above 15 bara is sufficiently high to avoid excessive production of flash vapours upon depressurizing to the initial pressure of between 1 and 2 bara.

The invention is of particular benefit in embodiments wherein the raw liquefied stream 1 comprises between 1 mol% and 1.8 mol% of nitrogen.

In the embodiment of Figure 1, the cryogenic hydrocarbon composition 8 is passed directly into the liquid hydrocarbon product line 90. In the embodiments of Figures 2 and 3, only a non-flashed fraction of the cryogenic hydrocarbon composition 8 is discharged into the liquid hydrocarbon product line 90 via the end flash separator 50.

A by-product vapour 60 is collected from the cryogenic hydrocarbon composition 8. This may suitably comprise collecting boil-off gas from the cryogenic storage tank 210, possibly via the boil-off gas supply line 230 if such line is provided. Boil-off gas results from adding heat to at least part of the cryogenic hydrocarbon composition, whereby a part of said methane-containing liquid phase evaporates to form said boil-off gas. In embodiments comprising the optional end flash separator 50, the collecting of the by-product vapour 60 may instead or in addition to collecting boil-off gas comprise collecting of the flash vapour from the end flash separator 50 via the flash vapour line 64.

The such collected by-product vapour 60 is then compressed to a treatment pressure in the range of between 2 and 15 bar absolute, thereby obtaining a compressed vapour 70 in the compressed vapour discharge line 70 at the compressor discharge outlet 261 of the by-product compressor 260.

The compressed vapour 70 is passed through the condensing heat exchanger train 235, thereby forming a partially condensed intermediate stream from the compressed vapour 70. The partially condensed intermediate stream comprises a condensed fraction and a vapour fraction. The partially condensed intermediate stream is formed by partially condensing the compressed vapour 70 by heat exchanging the compressed vapour 70 against at least the auxiliary refrigerant stream 132, whereby heat is passed from the compressed vapour 70 to the auxiliary refrigerant stream 132 at a cooling duty.

Optionally, heat is also passed to supplementary refrigerating streams, such as for instance the supplemental refrigerant stream 142 and/or the off gas conveyed in the vapour fraction discharge line 80.

The partially condensed intermediate stream is separated into the condensed fraction and the vapour fraction, at a separation pressure of between 2 and 15 bar absolute. To this end, the partially condensed intermediate stream may be passed to the first gas/liquid separator 33. The vapour fraction is discharged from the first gas/liquid separator via the vapour fraction discharge line 80 as off gas. The vapour fraction 80 has a selected heating value. The heating value may be selected according to a heating demand.

Suitably, at least a fuel portion of the vapour fraction 80 is passed to the combustion device 220 at a fuel gas pressure that is not higher than the separation pressure.

The cooling duty in the condensing heat exchanger 35 is automatically adjusted to regulate the heating value of the vapour fraction 80 being discharged. In embodiments wherein the vapour fraction 80 is passed to one or more selective consumers of methane, such as for instance the combustion device 220 shown in Figure 1, the controlling can be done in response to the demanded heating power, whereby the partial flow rate of methane is controlled to achieve a heating value that matches the demand. Suitably, the auxiliary refrigerant stream flow control valve 135 may be controlled by the pressure controller PC to maintain a predetermined target flow rate of auxiliary refrigerant stream 132 through the condensing heat exchanger 35. The actual pressure in the vapour fraction discharge line 80 is causally related to the heating value that is being regulated. The pressure controller PC will be set to decrease the open fraction of the auxiliary refrigerant stream flow control valve 135 when the pressure drops below a pre-determined target level, which is indicative of a higher consumption rate of methane than supply rate in the vapour fraction 80. Conversely, the pressure controller PC will be set to increase the open fraction of the auxiliary refrigerant stream flow control valve 135 when the pressure exceeds the pre-determined target level.

The vapour fraction 80 is envisaged to contain between from 30 mol% to 90 mol% of nitrogen, preferably between from 30 mol% to 70 mol% of nitrogen or between from 45 mol% to 90 mol% of nitrogen, more preferably between from 30 mol% to 60 mol% of nitrogen, still more preferably from 45 mol% to 70 mol% of nitrogen, most preferably from 45 mol% to 60 mol% of nitrogen.

To achieve a content of nitrogen of around 60 mol%, sufficient methane must be recondensed from the by-product vapour stream. It has been found that this can be done using a pressure of the compressed vapour stream of between 4 and 8 bara, and achieving a temperature of the partially condensed intermediate stream of between from -150 °C to -135 °C.

Going back to the first gas/liquid phase separator 33, the condensed fraction is discharged from the first gas/liquid separator 33 through the condensed fraction discharge line 40. Typically, the condensed fraction is expected to comprise less than 10 mol% of nitrogen. At higher nitrogen content, cryogenic hydrocarbon composition in the cryogenic storage tank 210 may have a nitrogen content exceeding a desired maximum of about 1.1 mol%. A depressurized recycle portion is formed from the condensed fraction in the condensed fraction discharge line 40 by depressurizing the condensed fraction to a pressure not lower than the initial pressure. The depressurized recycle portion is then injected into the cryogenic hydrocarbon composition, for instance via the injection point 48 into the cryogenic hydrocarbon composition 8, via the end flash separator 50, or even directly into the liquid hydrocarbon product line 90.

The auxiliary refrigerant 132 stream preferably has a bubble point under standard conditions at a lower temperature than the bubble point of the overhead vapour stream 70 under standard conditions (ISO 13443 standard: 15 °C under 1.0 atmosphere absolute pressure). This facilitates recondensing a relatively high amount of the methane that is present in the by-product vapour stream 60, which in turn facilitates the controllability of the methane content in the vapour fraction 80. For instance, the auxiliary refrigerant may contain between from 5 mol% to 75 mol% of nitrogen. In a preferred embodiment, the auxiliary refrigerant stream is formed by a slip stream of the main refrigerant stream, more preferably by a slip stream of the light refrigerant fraction. This latter case is illustrated in Figure 3, but may also be applied in the embodiment of Figures 1 and 2. Such a slip stream may conveniently be passed back into the main refrigerant circuit via the shell side 186 of the cryogenic heat exchanger 180, where it may still assist in withdrawing heat from the stream in the upper and/or lower tube bundles.

In one example, a contemplated composition of the auxiliary refrigerant contains between 25 mol% and 40 mol% of nitrogen; between 30 mol% and 60 mol% of methane and up to 30 mol% of C_2 (ethane and/or ethylene), whereby the auxiliary refrigerant contains at least 95% of these constituents and/or the total of nitrogen and methane is at least 65 mol%. A composition within these ranges is may be readily available from the main refrigerant circuit if a mixed refrigerant is employed for sub-cooling of the liquefied hydrocarbon stream.

It is also possible to employ a separate refrigeration cycle for the purpose of partially condensing the compressed vapour stream 70. However, employing a slip stream from the main refrigerant stream has as advantage that the amount of additional equipment to be installed is minimal. For instance, no additional auxiliary refrigerant compressor and auxiliary refrigerant condenser would be needed.

Preferably, the separation pressure is in the range of from 4 to 8 bara, which pressure meets the requirements of a low-pressure fuel gas stream suitable for conveying the off gas to the combustion device 220 without need for further compression. A higher pressure may be selected if the combustion device 220 is at a relatively large distance from the first gas/liquid phase separator, under which circumstances an additional pressure drop may be expected in the course of conveying the off gas to the combustion device 220.

Preferably, the treatment pressure exceeds the separation pressure by more than about 1 bar to allow for a pressure drop caused by passing the compressed vapour 70 through the condensing heat exchanger train 235, but preferably not by more than 5 bar since that would require unnecessary compression power on the by-product compressor 260.

In some embodiments, the target amount of nitrogen dissolved in the liquid hydrocarbon product stream 90 is between 0.5 and 1 mol%, preferably as close to 1.0 mol% as possible yet not exceeding 1.1 mol%.

Elements of the various configurations of the condensing heat exchanger train 235 that have been described above with reference to Figures 1 to 3 may be combined to form new embodiments.

As an example, Figure 4 shows an embodiment wherein the condoning heat exchanger train 235, in addition to the condensing heat exchanger 35, comprises three supplemental condensing heat exchangers: one in the form of a flash vapour cold recovery heat exchanger 36; one in the form of the off gas cold recovery heat exchanger 85; and one ambient heat exchanger 38. The flash vapour cold recovery heat exchanger 36 is configured adjacent to the condensing heat exchanger 35, whereby the compressed vapour 70 is arranged in indirect heat exchanging contact with the flash vapour line 64. Configured adjacent to the flash vapour cold recovery heat exchanger 36 is the off gas cold recovery heat exchanger 85, wherein the compressed vapour 70 is arranged in indirect heat exchanging contact with the vapour fraction line 80. Adjacent to the off gas cold recovery heat exchanger 85 and, on the other side, to the compressor discharge outlet 261 of the by-product compressor 260, is configured a third supplemental condensing heat exchanger in the form of the ambient heat exchanger 38. The ambient heat exchanger 38 can be in the form of an air serviced heat exchanger, in which a stream of ambient air is configured in indirect heat exchanging contact with the compressed vapour line 70, or a water serviced heat exchanger in which a stream of water is configured in indirect heat exchanging contact with the compressed vapour line 70. In the same way as shown with reference to Figure 3, the source of auxiliary refrigerant 132 for the condensing heat exchanger 35 may be the LMR line 131 of the main refrigerant circuit 101 (shown in Fig. 3, but not shown in Fig. 4). The second LMR return line 138 on an upstream end thereof fluidly connects with the auxiliary refrigerant line 132 via the condensing heat exchanger 35 and on the downstream end thereof it ultimately connects with the spent refrigerant line 150 (not shown in Fig. 4).

The remaining elements shown in Figure 4, and optional elements not shown in Figure 4, are identical to those described above with reference to Figs. 1 to 3 and will not be described again here. Similar to what is shown and described in the embodiment of Fig. 3, the cryogenic storage tank 210 may be located at a significant distance D removed from the by-product compressor 260.

Static simulations have been performed on the embodiment shown in Figure 3, assuming operation in holding mode (Tables 1 and 2) and in loading mode (Table 3). In all cases, the cryogenic hydrocarbon composition 8 was assumed to consist for more than 90 mol% of a mixture of nitrogen and methane (98.204 mol%). The example of Table 1 is a reference case wherein the amount of nitrogen is 0.77 mol% and methane 95.89 mol% making the total is more than 96.6 mol%. In the example of Table 4 the amount of nitrogen is higher, 1.53 mol%. The balance in both cases consists of a mixture of the group of C_2-C_4 alkanes consisting of ethane, propane, normal butane, and isobutene; and carbon dioxide. These constituents leave the process via the liquid hydrocarbon product stream 90.

Table 1: Reference nitrogen, holding mode; Reference numbers correspond to Figure 3.

Reference number	8	40	60	64	70	80	90	230
Phase (V/L)	V+L	L	V	V	V	V	L	V
Flow rate (kg-mol/s)	11.9	0.24	0.36	0.23	0.36	0.11	11.9	0.13
Temperature (°C)	-161	-140	-151	-162	-52	-140	-162	-66
Pressure (bara)	1.15	6.7	1.05	1.05	7.9	6.7	1.05	1.15
Nitrogen (mol%)	0.77	4.24	13.3	13.8	13.3	32.6	0.59	12.5
Methane (mol%)	95.9	95.8	86.7	86.2	86.7	67.4	96.1	87.5

The heating value in the off gas in this reference case was 62 MW, which was targeted to satisfy a boiler requirement for a selected heat transfer fluid unit during an average ambient temperature period. The selected heat transfer unit delivers process heat to a number of modules, including an inlet separator overhead gas heater, an acid gas removal unit reboiler, and fractionation train reboilers, in a selected liquefaction system designed to deliver about 6 MTPA (mega tonne per annum) of liquefied natural gas.

Table 2: High nitrogen, holding mode; Reference number correspond to Figure 3.

Reference number	8	40	60	64	70	80	90	230
Phase (V/L)	V+L	L	V	V	V	V	L	V
Flow rate (kg-mol/s)	10.3	0.30	0.44	0.32	0.44	0.13	10.3	0.12
Temperature (°C)	-163	-146	-157	-164	-61	-146	-164	-65
Pressure (bara)	1.15	6.7	1.05	1.05	7.9	6.7	1.05	1.15
Nitrogen (mol%)	1.53	8.24	22.0	22.5	22.0	53.0	1.07	20.6
Methane (mol%)	97.9	91.8	78.0	77.5	78.0	47.0	98.3	79.4

The compressor power consumed by the by-product compressor 260 was 1.1 MW in the reference nitrogen case versus 1.3 MW in the high nitrogen case. The consumed cooling duty in the reference nitrogen case was 2.8 MW (1.0 MW in the slip stream heat exchanger 37 and 1.8 MW in the condensing heat exchanger 35), while in the high nitrogen case 3.5 MW was used (1.1 MW in the slip stream heat exchanger 37 and 2.4 MW in the condensing heat exchanger 35).

The heating value provided in the off gas 80 in the high nitrogen case was 50 MW. This was targeted to operate the same liquefaction system as assumed for the reference case simulation, but at a higher ambient temperature (summer period) rather than average ambient temperature. Of course, at higher ambient temperature the process heat requirement is lower. It is interesting to note that the lower heating power requirement was matched by the line up of Figure 3, even though more nitrogen needed to be discharged via the off gas. The amount of nitrogen in the liquid hydrocarbon stream 90 was still within the maximum allowed limit of 1.1 mol%.

Likewise, it is found to be possible to regulate the heating value with the same line up to about 80 MW to satisfy the process heat requirements in winter period.

Table 3 summarizes results of simulations of the high nitrogen case corresponding to Table 2, in loading mode. The calculation assumed an additional boil off gas supply rate of 0.7 mol% of the LNG being transferred to the ship.

Table 3: High nitrogen, loading mode; Reference number correspond to Figure 3.

Reference number	8	40	60	64	70	80	90	230
Phase (V/L)	V+L	L	V	V	V	V	L	V
Flow rate (kg-mol/s)	10.3	0.38	0.52	0.34	0.52	0.14	10.3	0.18
Temperature (°C)	-163	-147	-153	-164	-53	-147	-164	-70
Pressure (bara)	1.15	6.7	1.05	1.05	7.9	6.7	1.05	1.15
Nitrogen (mol%)	1.53	9.04	22.0	23.0	22.0	56.1	1.10	20.0
Methane (mol%)	97.5	90.96	78.0	77.0	78.0	43.9	98.3	80.0

The cooling duty in the condensing heat exchanger was adjusted to 3.0 MW to maintain the same heating value of 50 MW in the vapour fraction 80. Also the cooling duty in the slip stream heat exchanger 37 increased compared to the holding mode case of Table 3, to 1.45 MW, due to a few degrees warmer by-product vapour in by-product vapour line 60.

Table 4 summarizes results of simulations that have been performed on the embodiment shown in Figure 4, assuming operation in holding mode. In this case the composition of the cryogenic hydrocarbon composition 8 was the same as in the reference case which forms the basis for Table 1. A conveyor compressor was configured in the boil-off gas supply line 230, at the site of the cryogenic storage tank 210. The ambient heat exchanger 38 was assumed to be a water cooler.

Table 4: Reference nitrogen, holding mode; Reference numbers correspond to Figure 4.

Reference number	8	40	60	64	70	80	90	230
Phase (V/L)	V+L	L	V	V	V	V	L	V
Flow rate (kg-mol/s)	11.9	0.24	0.36	0.23	0.36	0.11	11.9	0.13
Temperature (°C)	-161	-140	-45	-162	+127	-140	-162	-66
Pressure (bara)	1.15	6.7	1.05	1.05	7.9	6.7	1.05	1.15
Nitrogen (mol%)	0.77	4.24	13.3	13.8	13.3	32.5	0.59	12.5
Methane (mol%)	95.9	95.8	86.7	86.2	86.7	67.5	96.1	87.5

The by-product compressor power in the case of Table 4 was 2.2 MW, compared to 1.1 MW in the case of Table 1, which difference is attributed to the fact that the temperature of the by-product vapour 60 is higher in the case of Table 4 as a result of which the density is lower. This is because the flash vapour stream 64 and the boil off vapour stream 230 are used for cooling the compressed vapour 70. However, only 2.1 MW of cooling duty is used from the main cryogenic refrigerant circuit compared to 2.8 MW for the case of Table 1. The temperature of the compressed vapour 70 obtained from the by-product compressor 260 is first brought down to +21°C by dissipating 1.4 MW of duty to the ambient water; followed by transferring 0.6 MW of duty to the boil-off gas by indirect heat exchanging in the off gas cold recovery heat exchanger 85 thereby bringing the temperature of the compressed vapour stream 70 down to -29 °C; followed by transferring 1.0 MW of duty to the flash vapour 64 in the flash vapour cold recovery heat exchanger 36 by indirect heat exchanging against the flash vapour stream 64 thereby bringing the temperature of the compressed vapour stream 70 down to -109 °C; followed by the final condensing heat exchanging in the condensing heat exchanger 35 against the auxiliary refrigerant stream 132 in the form of the slip stream of the light refrigerant fraction from the liquefaction system 100 to bring the temperature down to -139 °C using 2.1 MW. This is the only external refrigeration duty needed for the partial condensation of the compressed vapour stream 70.

Finally, the limits of operation of the invention have been investigated by further simulations using the embodiment of Figure 4. Results are summarized in Table 5. Cases 1 to 5 investigate how the invention can work for increasing amounts of nitrogen in the cryogenic hydrocarbon composition 8, while maintaining a constant heating duty of 62 MW in the vapour fraction 80 off gas. It can be seen that the heating duty can be maintained by increasing the cooling duty in the condensing heat exchanger 35 (reflected in Table 5 by a lower temperature in the first gas/liquid separator 33). At 1.8 mol% nitrogen in the cryogenic hydrocarbon composition 8 the amount of nitrogen in the liquid hydrocarbon product stream 90 starts to exceed the maximum upper limit of about 1.1 mol%. Thus, the invention works for nitrogen contents in the raw liquefied product of up to about 1.8 mol%, for instance 1.7 mol%.

Table 5: 8 cases using line up of Figure 4.

Case number	1	2	3	4	5	6	7	8
Nitrogen in stream 8 (mol%)	0.51	1.01	1.50	1.80	1.99	1.80	1.80	1.80
Heating duty stream 80 (MW)	62	62	62	62	62	47	33	33
Nitrogen in stream 90 (mol%)	0.41	0.74	1.03	1.20	1.30	1.23	1.29	1.32
Nitrogen in stream 40 (mol%)	2.80	5.50	7.91	9.29	10.2	11.2	14.1	16.1
Nitrogen in stream 80 (mol%)	22.9	40.0	51.6	56.9	59.8	62.3	68.5	68.0
Temperature in separator 33 (°C)	-137	-142	-145	-147	-148	-149	-152	-146
Separation pressure (bara)	6.7	6.7	6.7	6.7	6.7	6.7	6.7	9.7

Cases 6 and 7 demonstrate that the heating duty in the off gas can be brought down by increasing the cooling duty in the condensing heat exchanger. However, this is at the penalty of re-condensing more nitrogen which ends up in the liquid hydrocarbon product stream 90.

Comparing cases 7 and 8 reveals that the cooling duty in the condensing heat exchanger can be reduced by increasing the pressure of the compressed vapour stream 70 (which allows a higher separation pressure in the first gas/liquid separator 33).

The person skilled in the art will understand that the present invention can be carried out in many various ways without departing from the scope described herein.

CLAIMS

1. Method of removing nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase, the method comprising:

- providing a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase at an initial pressure of between 1 and 2 bar absolute;
- collecting a by-product vapour from the cryogenic hydrocarbon composition;
- compressing said by-product vapour to a treatment pressure in the range of between 2 and 15 bar absolute, thereby obtaining a compressed vapour;
- forming a partially condensed intermediate stream from the compressed vapour comprising a condensed fraction and a vapour fraction, said forming comprising partially condensing the compressed vapour by heat exchanging the compressed vapour against an auxiliary refrigerant stream and thereby passing heat from the compressed vapour to the auxiliary refrigerant stream at a cooling duty;
- separating the condensed fraction from the vapour fraction in a first gas/liquid separator, at a separation pressure of between 2 and 15 bar absolute;
- discharging the vapour fraction from the first gas/liquid separator as off gas, said vapour fraction having a heating value;
- discharging the condensed fraction of the first gas/liquid separator;

- depressurizing the condensed fraction to a pressure not lower than the initial pressure, thereby forming a depressurized recycle portion;
- injecting the depressurized recycle portion into the cryogenic hydrocarbon composition;
- adjusting the cooling duty to regulate the heating value of the vapour fraction being discharged from the first gas/liquid separator.

2. The method according to claim 1, further comprising passing the vapour fraction to a combustion device at a fuel gas pressure not higher than the separation pressure.

3. The method according to claim 1 or 2, wherein the by-product vapour from the cryogenic hydrocarbon composition comprises boil-off gas obtained by adding heat to at least part of the cryogenic hydrocarbon composition whereby a part of said methane-containing liquid phase evaporates to form said boil-off gas.

4. The method according to any one of claims 1 to 3, wherein said providing of said cryogenic hydrocarbon composition comprises:

- heat exchanging a feed stream containing a hydrocarbon containing feed vapour in a cryogenic heat exchanger against a main refrigerant stream, thereby liquefying the feed vapour of the feed stream to provide a raw liquefied stream; and
- obtaining the cryogenic hydrocarbon composition from the raw liquefied stream.

5. The method according to claim 4, wherein said obtaining the cryogenic hydrocarbon composition from said liquefied stream comprises depressurizing the raw liquefied stream from a liquefaction pressure to the initial pressure.

6. The method according to claim 5, wherein a flash vapour is generated during said depressurizing, and wherein the by-product vapour from the cryogenic hydrocarbon composition comprises said flash vapour.

7. The method according to claim 6, wherein the flash vapour is separated from the cryogenic hydrocarbon composition in a second gas/liquid separator.

8. The method according to claim 7, wherein the raw liquefied stream passes in depressurized form to the second gas/liquid separator and wherein said injecting the depressurized recycle portion to the cryogenic hydrocarbon composition is performed by injecting the depressurized recycle portion into one of the group consisting of the liquefied stream in depressurized form as it passes to the second gas/liquid separator and the second gas liquid separator.

9. The method according to any one of claims 4 to 8, wherein the auxiliary refrigerant stream is formed by a slip stream of the main refrigerant stream.

10. The method according to any one of claims 1 to 9, wherein the auxiliary refrigerant stream contains between from 5 mol% to 75 mol% of nitrogen.

11. The method according to any one of claims 1 to 10, wherein the vapour fraction comprises between from 30 mol% to 90 mol% of nitrogen.

12. The method according to any one of claims 1 to 11, wherein the condensed fraction comprises less than 10 mol% of nitrogen.

13. The method according to any one of claims 1 to 12, wherein the temperature of the partially condensed intermediate stream is between from -150 °C to -135 °C.

14. The method according to any one of claims 1 to 13, wherein the first gas/liquid separator represents essentially a single equilibrium stage wherein vapour and liquid inside the gas/liquid separator are in thermodynamic equilibrium.

15. An apparatus for removing nitrogen from a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase, the apparatus comprising:

- a holder for a cryogenic hydrocarbon composition comprising nitrogen and a methane-containing liquid phase at an initial pressure;
- a by-product vapour line fluidly connected to the holder and arranged to collect a by-product vapour from the holder;
- a by-product compressor arranged in the by-product vapour line arranged to compress at least said by-product vapour to a treatment pressure that exceeds the initial pressure to provide a compressed vapour at a compressor discharge outlet of the by-product compressor;
- at least one condensing heat exchanger in fluid communication with the compressor discharge outlet and arranged to receive the compressed vapour and to form partially condensed intermediate stream out of the compressed vapour, the partially condensed intermediate stream comprising a condensed fraction and a vapour fraction, and said condensing heat exchanger furthermore arranged to bring the compressed vapour in a heat exchanging contact with an auxiliary refrigerant stream whereby during operation heat passes from the compressed vapour to the auxiliary refrigerant stream at a cooling duty;

- a first gas/liquid separator arranged to receive the partially condensed intermediate stream and to separate the condensed fraction from the vapour fraction at a separation pressure;
- a vapour fraction discharge line fluidly connected to the first gas/liquid separator, arranged to convey the vapour fraction away from the first gas/liquid separator;
- a condensed fraction discharge line arranged to convey the condensed fraction away from the first gas/liquid separator, said condensed fraction discharge line on an upstream end thereof fluidly connected to the first gas/liquid separator and on a downstream end thereof in fluid communication with an injection point in confluence with the cryogenic hydrocarbon composition;
- a depressurizing system disposed in the condensed fraction discharge line, arranged to depressurize the condensed fraction to a pressure not lower than the initial pressure, thereby forming a depressurized recycle portion;
- a cooling duty controller arranged to adjust the cooling duty to regulate a heating value of the vapour fraction being discharged from the first gas/liquid separator.

16. The apparatus of claim 15, wherein the first gas/liquid separator consists of a drum free from internals forming a vapour/liquid contacting section.

17. The apparatus according to claim 15 or 16, wherein the first gas/liquid separator represents essentially a single equilibrium stage wherein vapour and liquid inside the gas/liquid separator are in thermodynamic equilibrium.

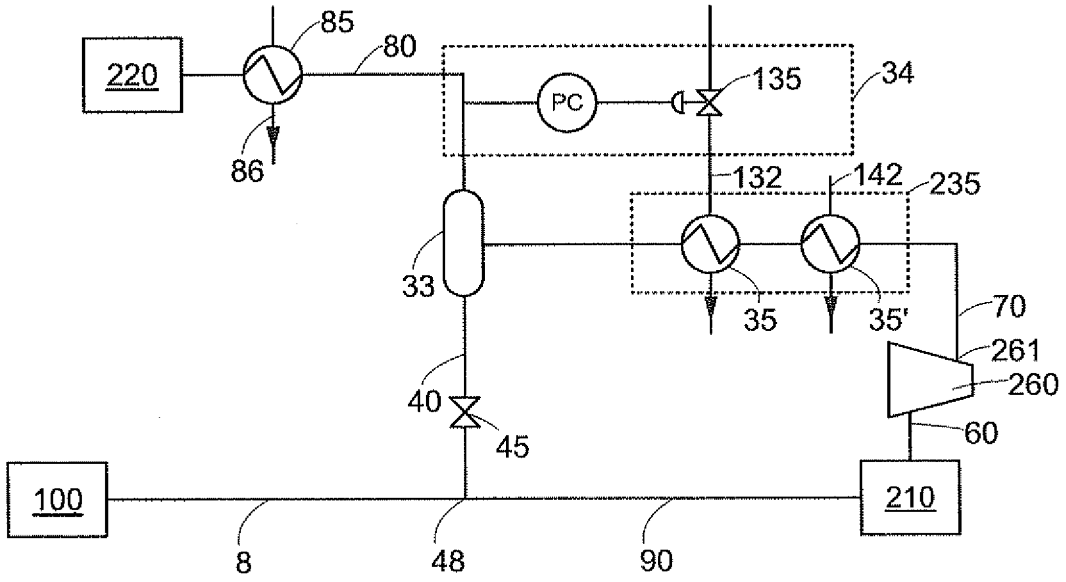
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FIG. 1

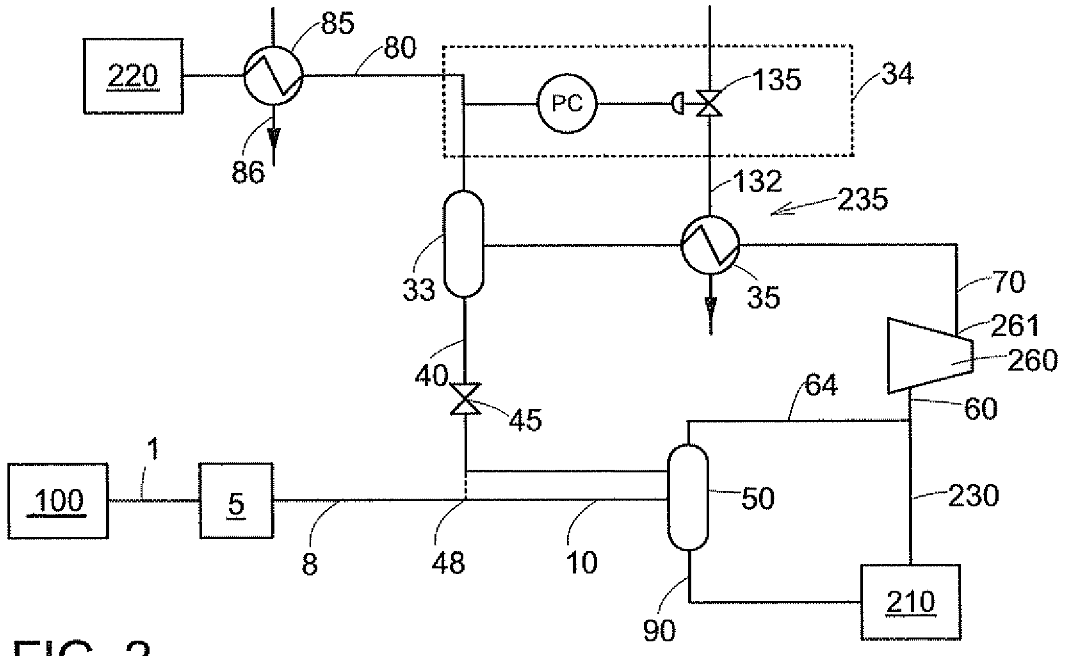
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FIG. 2

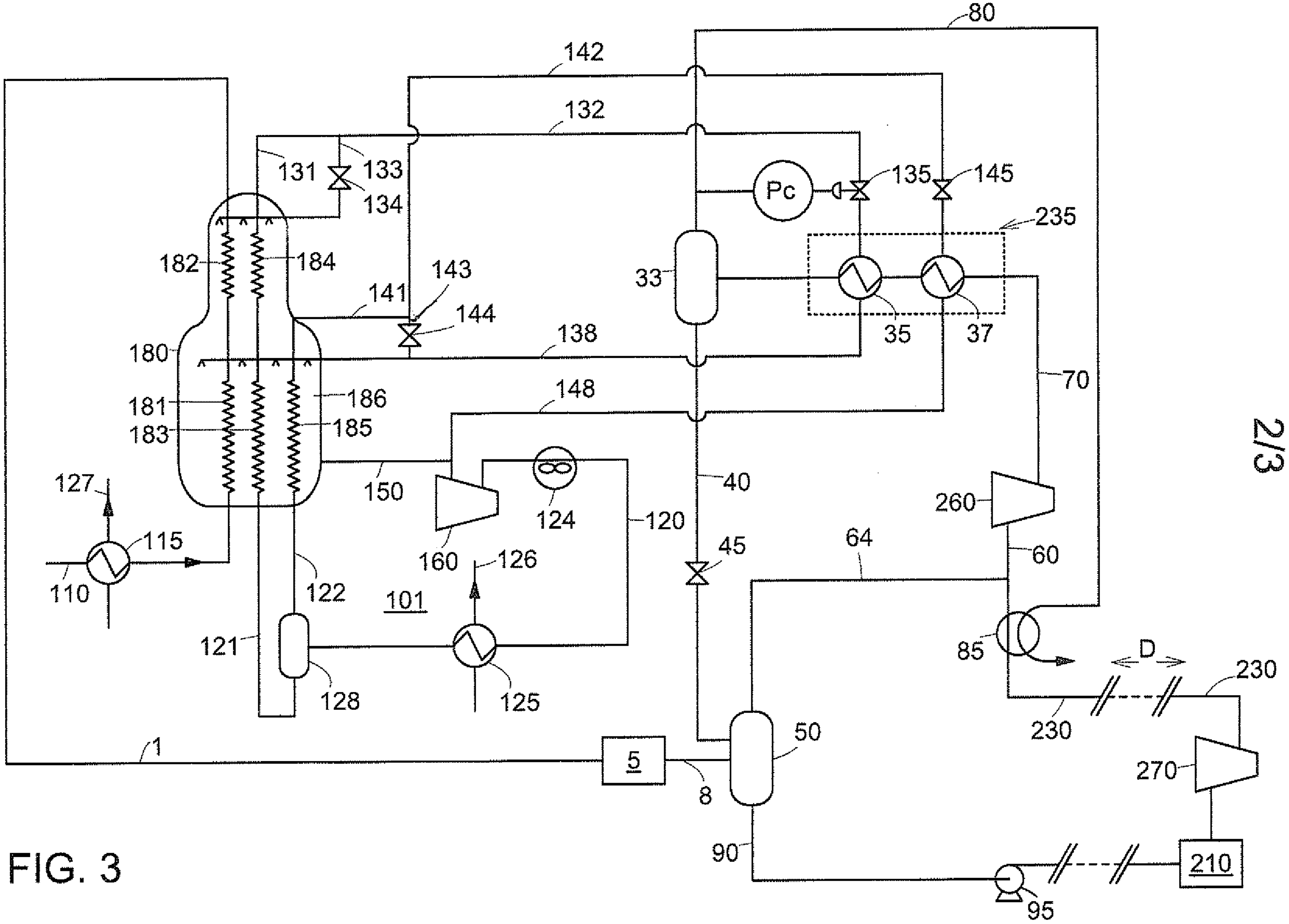
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FIG. 3

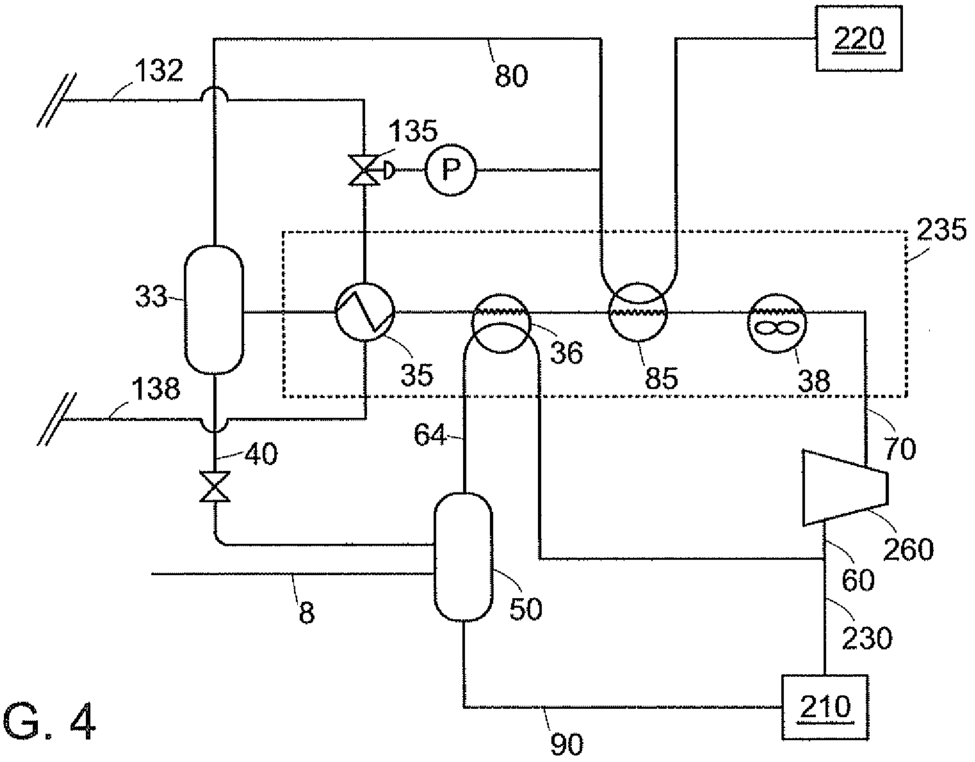
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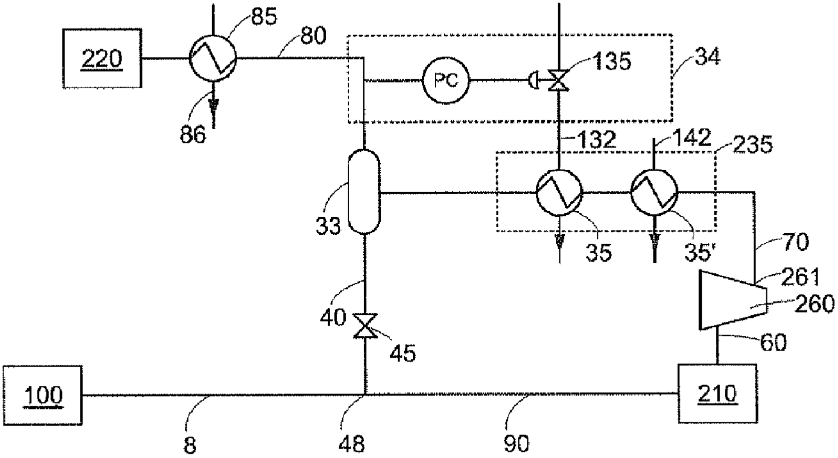
FIG. 4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