

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2008322758 B2**

- (54) Title
Method for initiating a cooling cycle with a hydrocarbon mixture
- (51) International Patent Classification(s)
F25J 1/02 (2006.01) **F25B 45/00** (2006.01)
F25B 9/00 (2006.01)
- (21) Application No: **2008322758** (22) Date of Filing: **2008.09.02**
- (87) WIPO No: **WO09/063142**
- (30) Priority Data
- (31) Number (32) Date (33) Country
07 06 182 **2007.09.04** **FR**
- (43) Publication Date: **2009.05.22**
(44) Accepted Journal Date: **2012.05.17**
- (71) Applicant(s)
TOTAL S.A.
- (72) Inventor(s)
Chretien, Denis
- (74) Agent / Attorney
Griffith Hack, GPO Box 1285, Melbourne, VIC, 3001
- (56) Related Art
US 6357257 B1
US 5711158 A

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété Intellectuelle
Bureau international



(10) Numéro de publication internationale
WO 2009/063142 A3

(43) Date de la publication internationale
22 mai 2009 (22.05.2009)

- (51) Classification internationale des brevets :
F25J 1/02 (2006.01) F25B 45/00 (2006.01)
F25B 9/00 (2006.01)
- (21) Numéro de la demande internationale :
PCT/FR2008/001223
- (22) Date de dépôt international :
2 septembre 2008 (02.09.2008)
- (25) Langue de dépôt : français
- (26) Langue de publication : français
- (30) Données relatives à la priorité :
07 06 182 4 septembre 2007 (04.09.2007) FR
- (71) Déposant (pour tous les États désignés sauf US) :
TOTAL S.A. [FR/FR]; 2, place Jean Millier, La Défense
6, F-92400 Courbevoie (FR).
- (72) Inventeur; et
- (75) Inventeur/Déposant (pour US seulement) : CHRETIEN,
Denis [FR/FR]; 8, rue Santerre, F-75012 Paris (FR).
- (74) Mandataire : POCHART, François @; Cabinet Hirsch
& Associés, 58, avenue Marceau, F-75008 Paris (FR).
- (81) États désignés (sauf indication contraire, pour tout titre
de protection nationale disponible) : AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,

CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ,
EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG,
SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) États désignés (sauf indication contraire, pour tout titre
de protection régionale disponible) : ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), eurasién (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), européen (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Déclarations en vertu de la règle 4.17 :

— relative à la qualité d'inventeur (règle 4.17.iv))

Publiée :

- avec rapport de recherche internationale (Art. 21(3))
— avant l'expiration du délai prévu pour la modification des
revendications, sera republiée si des modifications sont
reçues (règle 48.2.h))

[Suite sur la page suivante]

(54) Title : METHOD FOR INITIATING A COOLING CYCLE WITH A HYDROCARBON MIXTURE

(54) Titre : PROCÉDE DE DEMARRAGE D'UN CYCLE DE REFRIGERATION A MELANGE D'HYDROCARBURES

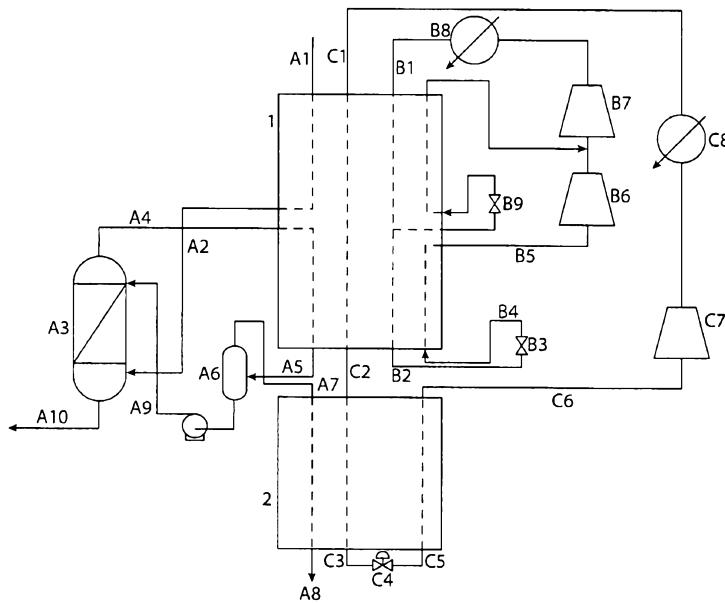


Figure 1

(57) Abstract : The invention relates to a method for starting a natural gas liquefaction unit comprising a cooling circuit that contains a refrigerant containing a hydrocarbon mixture, wherein said method consecutively comprises: (a) injecting and purging a cleaning gas in the cooling circuit; (b) injecting a first filler gas into the cooling circuit; and (c) injecting a second filler gas into the cooling circuit; wherein the average molar mass of the first filler gas is higher than the average molar mass of the second filler gas. The invention also relates to an associated method for liquefying natural gas.

(57) Abrégé : L'invention concerne un procédé de démarrage d'une unité de liquéfaction de gaz naturel comprenant un circuit de réfrigération contenant un fluide frigorigène qui comprend un mélange d'hydrocarbures, dans lequel le procédé comprend successivement : (a) l'injection et la purge d'un gaz de nettoyage dans le circuit de réfrigération;

(b) l'injection d'un premier gaz de remplissage dans le circuit de réfrigération; et (c) l'injection d'un deuxième gaz de remplissage dans le circuit de réfrigération; la masse molaire moyenne du premier gaz de remplissage étant supérieure à la masse molaire moyenne du deuxième gaz de remplissage. L'invention concerne également un procédé de liquéfaction de gaz naturel associé.

WO 2009/063142 A3

WO 2009/063142 A3



**(88) Date de publication du rapport de recherche
internationale :**

23 décembre 2009

**METHOD OF STARTING UP A COOLING CYCLE CONTAINING A
HYDROCARBON MIXTURE**

5 **TECHNICAL FIELD**

The invention relates to a method of starting up a cooling cycle containing a mixture of hydrocarbons. The invention also relates to a method for liquefying natural gas using this starting-up method.

10 **TECHNICAL BACKGROUND**

Liquefaction of natural gas requires its cooling by a cooling unit down to a cryogenic temperature of -155°C during liquefaction and then down to -162°C in the storage tank, after its expansion at atmospheric pressure. The cooling unit generally comprises a refrigeration cycle (or circuit) or a succession of refrigeration cycles (or
15 circuits) operating by condensation-expansion-evaporation-compression. Refrigerant fluids used in refrigeration cycles may be pure substances (cascade cycle, Conoco Phillips Optimized CascadeTM method), mixtures (Axens LiquefinTM method, Linde Mixed Fluid CascadeTM) or further a combination of both (APCI C3-MR cycle). All these cycles are well known to one skilled in the art.

20 Non-azeotropic mixtures of components having different boiling points and in particular mixtures of hydrocarbons (possibly in combination with other components) are notably frequently used in one or more refrigeration cycles.

During the first operation of the cooling unit as well as subsequently to each stopping of the unit (for example for maintenance), a particular procedure for starting
25 up the cooling unit has to be followed. Taking the example of a cooling unit with two cycles, i.e. a pre-refrigeration cycle and a refrigeration cycle, the latter containing a refrigerant fluid mainly comprising a methane/ethane mixture, the conventional procedure consists of:

- sweeping all the circuits with a cleaning gas called « defrost gas », which
30 is generally clean and dry natural gas, originating from the treatment and drying units upstream from the cryogenics, or else with nitrogen, notably in order to remove any trace of water in the circuit;
- filling the pre-refrigeration cycle with the suitable refrigerant fluid (for example pure propane or ethane and propane) and operating (putting into
35 a cold state) the pre-refrigeration cycle;
- filling the refrigeration cycle with natural gas (generally the « defrost gas ») until the desired amount of methane is obtained in the cycle;

- filling the refrigeration cycle with ethane until the desired amount of ethane is obtained in the cycle;
- if necessary, completing the filling of the cycle by adding the other minority components to the refrigerant fluid.

5 This conventional starting-up procedure poses a certain number of problems. First of all, the condensation of the refrigerant fluid tends to be established with difficulty in the refrigeration cycle; furthermore an increase of pressure in the cycle, which would facilitate this condensation, cannot be contemplated unless the compressor is specifically modified to adapt it to the starting phase as well as to the
10 nominal operation. Consequently, operation of the refrigeration cycle takes a relatively long time. Another problem is that the temperature difference between the inlet and the outlet of the expander may for example reach 50-60°C. This temperature difference is too large for the mechanical strength of the parts, and in particular for the mechanical strength of the exchanger of the cycle. The latter is
15 therefore subject to significant risks of mechanical failure.

Therefore, there exists a real need for improving the starting-up method for a cooling unit, notably by facilitating condensation in the cycle in order to accelerate the process, and by reducing the amplitude of the temperature drop from one side of the expander of the refrigeration cycle to the other.

20

SUMMARY OF THE INVENTION

The invention first relates to a method for starting up a cooling unit comprising a refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons, wherein the method successively comprises:

- 25 (a) the injection and purge of a cleaning gas into the refrigeration circuit;
(b) the injection of a first filling gas into the refrigeration circuit; and
(c) the injection of a second filling gas into the refrigeration circuit;
the average molar mass of the first filling gas being greater than the average molar mass of the second filling gas.

30 According to one embodiment, the cooling unit is a natural gas liquefaction unit.

According to one embodiment, the first cleaning gas comprises at least 50 mol%, preferably at least 80 mol%, most preferably at least 90 mol%, ideally at least 95 mol%, of ethane.

35 According to one embodiment, the second filling gas preferably comprises at least 50 mol% of methane, most preferably at least 70 mol%, or even at least 80 mol% of methane.

According to one embodiment, the cleaning gas and/or the second filling gas are de-acidified and dried natural gas.

According to one embodiment, the aforementioned method comprises after step (a), and preferably after step (b), one or more steps of injecting additional filling gases into the refrigeration circuit, each additional filling gas preferably comprising nitrogen, propane, isobutane, n-butane, isopentane, n-pentane, ethylene, propylene or
5 a mixture thereof.

According to one embodiment, the first and the second filling gases provide at least 50%, preferably at least 60%, most preferably at least 70%, or even at least 80% of the molecules of refrigerant fluid present in the refrigeration circuit at the end of the starting-up method.

10 According to one embodiment, the refrigeration circuit comprises a heat exchanger comprising a hot inlet and a cold inlet and the temperature of the refrigerant fluid at the cold inlet of the heat exchanger decreases by at least 30°C, preferably by at least 40°C, more particularly by at least 50°C, or even by at least 60°C, between the beginning and the end of step (b).

15 According to one embodiment, the refrigeration circuit comprises a Joule-Thompson expansion valve comprising an inlet and an outlet and the temperature difference of the refrigerant fluid between said inlet and said outlet is less than 40°C, preferably less than 30°C, ideally less than 25°C, throughout the method.

20 According to one embodiment, the cooling unit further comprises a pre-refrigeration circuit and the pre-refrigeration circuit is set to nominal operation before step (b).

According to one embodiment, the cooling unit further comprises an additional refrigeration circuit.

25 According to one embodiment, the additional refrigeration circuit is a refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons, and the method comprises after step (c):

- (d) the injection of the first filling gas into the additional refrigeration circuit;
- (e) the injection of the second filling gas into the additional refrigeration circuit.

30 According to an alternative embodiment, said refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons is the only refrigeration circuit of the cooling unit.

The object of the invention is also a method for liquefying natural gas in a cooling unit comprising a refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons, wherein the method comprises:

- 35
- starting up the cooling unit, according to the aforementioned method; and then
 - cooling and liquefying natural gas in said cooling unit.

With the present invention, the drawbacks of the prior art may be overcome. More particularly, it provides a method for starting up a cooling unit, in which

condensation in the cycle is carried out more easily than according to the conventional method without having to specifically adapt the compressor. The starting-up method according to the invention is therefore faster than the conventional method. Moreover the amplitude of the temperature drop from one side of the expander of the refrigeration cycle to the other is reduced, which greatly limits the risk of mechanical failure, notably at the exchanger(s).

This is accomplished by reversing the filling order of the refrigeration cycle relatively to the conventional paradigm, i.e. by rather injecting the heavy components (in particular ethane) before the lightweight components (in particular methane).

According to certain particular embodiments, the invention also has the advantageous characteristics listed below.

- The temperature difference between the inlet and outlet of the expander remains less than 30°C, preferably less than 25°C, or even 20°C, throughout the whole duration of the starting-up method.
- The compressor discharge temperatures during starting-up are lower than in the prior art, so that the metallurgical constraints imposed to the compressor or the resort to an intermediate refrigerant are thereby limited.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram of a cooling unit enabling natural gas to be liquefied, a unit to which the invention may be applied.

Fig. 2 illustrates an exchange diagram within the exchanger 2 illustrated in **Fig. 1**, the cooling unit being used according to the method of Example 2. The amount of heat in MMkcal/h is shown on the X-axis, and the temperature in °C on the Y-axis. Curve 1 illustrates the sum of the hot flows (incoming lines C2 and A7), and curve 2 illustrates the cold flow (incoming line C5). The diagram corresponds to instant t2 of Example 2.

Fig. 3 illustrates an exchange diagram within the exchanger 2 illustrated in **Fig. 1**, the cooling unit being used according to the method of Example 2. The amount of heat in MMkcal/h is shown on the X-axis and the temperature in °C on the Y-axis. Curve 1 illustrates the sum of the hot flows (incoming lines C2 and A7), and curve 2 illustrates the cold flow (incoming line C5). The diagram corresponds to instant t5 of Example 2.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The invention is now described in more detail in a non-limiting way in the following description.

Natural gas liquefaction method

In a very simplified way and for the clarity of the discussion, a natural gas liquefaction unit (cooling unit) to which the invention may be applied is schematically described below (with reference to **Fig. 1**). This liquefaction unit is a unit with two cycles, and it comprises a primary heat exchanger 1 for carrying out pre-cooling (or pre-refrigeration) and a secondary heat exchanger 2 for carrying out liquefaction and subcooling. These exchangers may be wound exchangers or exchangers with plates in brazed aluminum.

The reference marks beginning with the letter A correspond to the components of the circuit of the natural gas which is treated in the unit; those beginning with the letter B correspond to the components of the pre-refrigeration cycle; and those beginning with the letter C correspond to the components of the refrigeration cycle (responsible for liquefaction and subcooling).

During normal operation, the natural gas, preferably de-acidified and dried beforehand (i.e. treated so as to separate water and acid gases such as H₂S and CO₂ therefrom), is introduced into the unit through natural gas feed conduit A1. It is pre-cooled by passing in exchanger 1. At the outlet of exchanger 1, the pre-cooled (partly condensed) natural gas is drawn through draw-off conduit A2 and introduced at the bottom of separation column A3 (« scrub column »), the purpose of which is to remove from the gas the heavier components (such as benzene for example) which may subsequently crystallize. These heavy components are recovered at the bottom of the column and removed through sampling conduit A10.

The gas leaves column A3 at the top through draw-off conduit A4 and passes again into primary exchanger 1 so as to be partly condensed again. At the output of exchanger 1, draw-off conduit A5 sends the partly condensed gas into drum A6, which achieves separation of a liquid fraction and of a vapor fraction. The liquid fraction A9 is compressed by a pump and is used as reflux in column A3. The vapor fraction A7 is introduced into secondary exchanger 2 where it is liquefied. The liquefied natural gas is recovered at the outlet conduit A8, at a typical temperature of about -155°C.

Pre-cooling in the primary exchanger 1 is carried out by means of a conventional pre-refrigeration cycle provided with compressors (in the embodiment shown here, first compressor B6 and second compressor B7), with condenser B8 and expanders (in the embodiment shown here, first expander B3 and second expander B9).

More specifically, this cycle comprises an inlet conduit B1 which feeds primary exchanger 1 with refrigerant fluid in a liquid form. The refrigerant fluid is subcooled upon passing through exchanger 1 (its temperature decreasing below that of the bubble point) and it is recovered at the outlet of exchanger 1 through outlet

conduit B2; it is then expanded by expander B3 and the expanded refrigerant fluid is introduced into exchanger 1 through inlet conduit B4. The expanded refrigerant fluid is then vaporized against subcooling of the compressed refrigerant fluid from inlet conduit B1, condensation of the fluid of circuit C and cooling of the natural gas. The vaporized refrigerant fluid is taken through outlet conduit B5 and compressed by passing through both compressors B6 and B7. The compressed fluid is then pre-condensed by condenser B8 and recycled into feed conduit B1.

According to the diagram shown here, provision is made for a second evaporation level, i.e. a bypass is provided within exchanger 1 for the fluid submitted to condensation. This bypass returns the fluid for evaporation in exchanger 1 after expansion by expander B9; at the outlet of the exchanger, the evaporated fluid is brought back into the main circuit at second compressor B7.

Both of these evaporation levels have been described here as an example, but the composition of the cycle and in particular the number of evaporation levels may vary to the extent appreciated by one skilled in the art.

Also, the cooling at the secondary exchanger 2 is obtained by means of a refrigeration cycle C, which is a conventional cycle provided with a compressor C7, a heat exchanger C8 and an expander C4.

More specifically, this cycle comprises inlet conduit C1 which is connected at the inlet of the primary exchanger 1 in order to allow condensation of the refrigerant fluid. The fluid is recovered at the outlet of exchanger 1 through transfer conduit C2 which feeds fluid in the liquid state (hot inlet) to secondary exchanger 2. It is subcooled in exchanger 2 down to the same typical temperature of about -155°C as the natural gas, and it is recovered at the outlet through conduit C3 which feeds it to expander C4. The low pressure fluid is introduced into exchanger 2 through inlet conduit C5 (cold inlet), and it is then vaporized against subcooling of the fluid from transfer conduit C2 and liquefaction of the natural gas. The vaporized fluid is taken through outlet conduit C6 and compressed while passing through compressor C7. The compressed fluid is then cooled in heat exchanger C8 and recycled to inlet conduit C1.

The expanders described above are preferably Joule-Thompson valves. The heat exchanger C8 and the condenser B8 described above may be water coolers or air coolers.

The method for liquefying natural gas according to the invention is characterized in that the cooling/liquefaction unit is started up according to the method of starting up the cooling unit according to the invention, which is described in more detail hereafter.

The liquefaction method may be the subject of many alternatives which will clearly appear to one skilled in the art. Thus, many modifications or many additions

known to one skilled in the art may be provided to the cooling unit described above. In particular, the liquefaction method according to the invention may be with one cycle, with two cycles (as described above) or with three cycles, provided that at least one refrigerant fluid used comprises a mixture of hydrocarbons (possibly associated with other components, for example nitrogen). Generally, it will be the fluid of the cold cycle which will comprise a mixture of hydrocarbons, whatever the nature of the pre-refrigeration cycle might be.

By « mixture of hydrocarbons », is meant a mixture of at least two compounds of formula C_mH_n , wherein m and n are two integers. The relevant hydrocarbons may be saturated or unsaturated, linear or branched. Preferably, m is less than or equal to 6, preferably less than or equal to 5. Preferably the mixture of hydrocarbons comprises ethane and methane, which ideally represent more than 50 mol%, more than 60 mol%, more of 70% or more of 80 mol% of the whole hydrocarbon mixture.

According to one embodiment of the method with a single refrigeration cycle, the refrigerant fluid may comprise nitrogen, ethylene, propylene, methane, ethane, propane, isobutane, n-butane, and possibly isopentane and/or n-pentane. Methane and ethane are preferably the major components.

According to one embodiment of the method with two refrigeration cycles, the refrigerant fluid of the pre-refrigeration cycle (cycle noted as B above) comprises ethane and propane, or according to one alternative pure propane, or according to another alternative pure propylene; and the refrigerant fluid of the main refrigeration cycle (cycle noted as C above) comprises a mixture of nitrogen, methane, ethane, and optionally propane and/or isobutane, n-butane, isopentane, n-pentane, ethylene, propylene. Methane and ethane are preferably the major components. For example the nitrogen content may be from 5 to 10%, the methane content from 30 to 50% and the ethane content from 40 to 60%.

According to one embodiment of the method with three refrigeration cycles, the method uses three cascaded cycles, the refrigerant fluid of each cycle comprising a mixture of hydrocarbons (and in particular possibly comprising the various components mentioned above). For example, the refrigerant fluid of the pre-refrigeration cycle may be a mixture of ethane and propane, whereas the refrigerant fluid of both of the other refrigeration cycles may respectively be a mixture of methane, ethane and propane, and a mixture of nitrogen, methane and ethane. In this case, the starting-up method according to the invention as described below may be applied to both of the latter refrigeration cycles.

According to one alternative embodiment of the method with three refrigeration cycles, the refrigerant fluid of the first refrigeration cycle is propane, the refrigerant fluid of the second refrigeration cycle comprises a mixture of hydrocarbons (and may

notably comprise the various components mentioned above) and the refrigerant fluid of the third refrigeration cycle comprises nitrogen. For example, the refrigerant fluid of the second cycle may comprise methane, ethane, and propane.

5 Method of starting up the cooling unit

By « starting-up method » is meant all the operations leading the cooling unit from the stopped state to the state of normal operation, i.e. the state in which the cooling unit has nominal operating and natural gas treatment parameters.

10 During the first start-up or during restarting after maintenance, water may have been introduced into the different circuits. It would freeze during cooling down notably at the exchangers, leading to their being blocked or damaged because of the ice volume increase relative to liquid water.

Therefore, the method of starting up the cooling unit comprises in a first phase, the drying of the circuits, i.e. in the two cycle mode described here, the drying of the 15 natural gas circuit A, of the pre-refrigeration cycle B and of the refrigeration cycle C. To do this, a sweep may for example be carried out with clean and dry natural gas, for example originating from treatment and drying units upstream from the cryogenics.

This cleaning gas or « defrost gas » is notably set into motion in the coldest refrigeration loop by compressor C7. This gas may for example be taken from inlet 20 A1 of the cooling unit or from the outlet of the drum A6 (this second possibility being preferred in order to avoid the presence of heavy components, notably aromatics). The « defrost gas » may be replaced with nitrogen which shall need to be purged entirely if the latter is not involved in the refrigerant mixture. Cleaning/drying is accomplished at a low flow rate and with a small compression height: it 25 corresponds to step (a) of the method which is mentioned in the summary of the invention. For example the pressure in the cycles may be from 1 to 5 bar (absolute). In order to purge the water, there is a permanent supply and a permanent purge of the cleaning gas during this phase of the method.

In the case (described here) where a pre-refrigeration circuit B is present, and 30 once the latter is dry, one proceeds with filling it with the suitable refrigerant fluid. The operating parameters of the pre-refrigeration circuits are then gradually established to their nominal values and the primary exchanger 1 is thus cooled down.

In a second phase, it is then possible to form the inventory of refrigeration cycle C into its different components (i.e. adding these components into the circuit) 35 in order to proceed with the cooling down of secondary exchanger 2.

To do this, according to the prior art procedure, the purge of the natural gas is interrupted so as to stop the sweep and to continue to feed the loop with this gas comprising methane in majority. When the methane inventory of the loop is formed,

one proceeds with injecting ethane and then, if need be, with injecting propane (and possibly other components) in order to reach the composition of the refrigerant mixture provided for the method. Lastly, if necessary, the required complement of nitrogen is added. As methane is one of the main components of the refrigerant fluid and of the « defrost gas », it is considered to be natural in the prior art to proceed according to this order of introduction. The components are partly liquefied in the refrigeration loop as they are gradually introduced.

Now, the « defrost gas », primarily comprising methane, is difficult to liquefy. To do this, either very low temperatures have to be reached, which are initially unavailable at the beginning of the cooling down of the exchanger, or the discharge pressure of compressor C7 needs to be increased significantly in order to liquefy the gas. Now, the compressor C7 is designed for compressing a mixture of hydrocarbons and nitrogen, the average molar mass of which is typically between 22 and 30 whereas that of the « defrost gas » is in the range from 17 to 19. In the case of centrifugal compressors, the compression ratios are proportional to the average molar mass of the compressed gas. Thus, the use of the compressor with a lower average molar mass than in normal operation, necessarily produces a lower discharge pressure whereas condensation of the « defrost gas » necessary for cooling down specifically requires higher condensation pressures. The consequences of this as mentioned in the introduction are design constraints for compressor C7, a difficult start-up procedure and a longer time for cooling down. Further, when liquefaction of the « defrost gas » is achieved in the circuit, one stumbles against another drawback: from one side of expander C4 to the other, the difference between the temperature of the fluid in conduit C3 and that of the fluid in conduit C5 (which is the result of the liquid/vapor equilibrium in C5) is considerably larger than the difference obtained during nominal operation. This is due to the fact that the « defrost gas » is notably lighter than the refrigerant fluid for which expander C4 and exchanger 2 are designed. As mentioned in the introduction, the temperature deviations between flows C3 and C5 may then reach 40, 50 or even 60°C and generate thermal stresses capable of damaging the exchangers used for liquefying the natural gas.

The inventors have identified that the various aforementioned drawbacks are related to the fact that during the cooling down phases, the « defrost gas » has a too low average molar mass.

On the other hand, according to the invention, the order in which the methane and ethane inventories are carried out in the refrigerating loop is reversed.

Thus, step (b) of the method of the invention consists of injecting into the refrigeration circuit a first filling gas and step (c) consists of injecting into the refrigeration circuit a second filling gas, the second filling gas having an average

molar mass less than (and not greater than, as in the state of the art) that of the first filling gas. Preferably, the first filling gas has a larger average molar mass than that of the refrigerant fluid in nominal operation. Preferably, the second filling gas has an average molar mass less than that of the refrigerant fluid in nominal operation.

5 Preferably, steps (b) and (c) provide more than 40 mol% (or more than 50 mol% or more than 60 mol% or more than 70 mol%) of all the molecules of the refrigerant fluid in nominal operation. Other filling gases may be injected in a lesser proportion into the cycle, either together or separately, in order to complete the making-up of the refrigerant fluid, for example propane, isobutane, n-butane, isopentane, n-

10 pentane, ethylene, propylene, nitrogen. Each additional injection may be carried out between steps (a) and (b), between steps (b) and (c) or after step (c).

By « average molar mass », is meant the mean between the molar masses of the different components of the relevant fluid, weighted by the molar proportion of each of its components. For example, if a gas contains 1/3 of molecules A with molar

15 mass M_A and 2/3 of molecules B with molar mass M_B , the average molar mass of the gas is equal to $(1/3)M_A + (2/3)M_B$.

Preferably, the first filling gas contains ethane in majority and the second filling gas contains methane in majority (this second filling gas may be natural gas or « defrost gas » for example taken from conduit A1 or preferably at the outlet of drum A6).

20 Thus, according to the invention, the gas used for cooling down first has a higher molar mass than that of the refrigerant fluid in normal operation and the average molar mass in the circuit then decreases as the methane is gradually injected until it reaches the nominal average molar mass. The drawbacks reported previously are then suppressed.

25 As the refrigerant fluid comprises during step (b) in majority components heavier than methane, for example ethane in majority, its condensation point is at a lower pressure. It is therefore easily condensable and may thus rapidly provide increased refrigeration by evaporation at low pressure and thereby accelerate the cooling down. Also as the average molar mass is higher than in normal operation, the

30 compressor at constant polytropic height is able to easily provide high pressure facilitating condensation. The high discharge pressures of the compressor are therefore easier to attain than in the prior art and, together, the required condensation pressure is lower. Finally, the temperature drop related to the expansion of the refrigerant liquid through valve C4 is reduced and no longer endangers the

35 mechanical integrity of the exchangers.

Reversing the order of injecting the components of the refrigerant fluid therefore has advantages for operating the compressor and the exchangers.

Limiting the compression rate by first injecting ethane has another advantage for the compressor. It is known that the higher the compression rate, the larger the increase in temperature during compression. The usual procedure, by using « defrost gas » as a means for lowering the temperature of the liquefaction unit, imposes particularly high pressures to achieve its partial condensation. These high pressures cause particularly high discharge temperatures which may impose metallurgical constraints to the compressor or require an intermediate refrigerant in order to limit the final discharge temperature. Whatever the case, overcosts are therefore avoided, by means of the starting-up procedure according to the invention.

The method described above in connection with a cooling unit with two cycles, may easily be adapted by one skilled in the art to a unit with one cycle or with three cycles. Thus, in the case of a single cycle refrigeration unit containing a mixture of hydrocarbons, the method consists of applying steps (a), (b) and (c) mentioned above without the pre-requisite of cooling down the pre-refrigeration cycle. Conversely, in the case of a three cycle unit, the cycles are successively cooled down according to the decreasing order of their nominal temperatures; each cycle comprising a refrigerant fluid based on a mixture of hydrocarbons (and more generally based on a non-azeotropic mixture of components with different boiling points) may be cooled down according to the succession of steps (a), (b) and (c) described above.

EXAMPLES

The following examples illustrate the invention without limiting it.

Example 1 – refrigerant fluids comprising a mixture of hydrocarbons

Examples of known processes for liquefying natural gas, using refrigerant fluids based on hydrocarbon mixtures are listed below. Each of these processes may be implemented according to the method of the invention. The compositions below are of course typical compositions, likely to vary depending on the practical cases of application (nature of the gas to be liquefied, ambient conditions...).

1) APCI process. This process comprises 2 cycles: a first pre-cooling cycle with propane and a second for liquefaction and subcooling. The refrigerant fluid of the second cycle has the following composition:

- nitrogen: 5.83 mol%;
- methane: 44.28 mol%;
- ethane: 37.30 mol%;
- propane: 21.59 mol%.

The second cycle of the method may be cooled down according to the succession of steps (a) and (c) described above.

2) Linde process. This process comprises three cycles, i.e. a pre-cooling cycle, a liquefaction cycle and a subcooling cycle. The refrigerant fluid of the subcooling cycle has the following composition:

- nitrogen: 8.93 mol%;
- 5 – methane: 54.88 mol%;
- ethane: 36.19 mol%.

The subcooling cycle may be cooled down according to the succession of steps (a) to (c) described above.

3) Incorporated cascade process. This process comprises a single refrigeration cycle. It is of the same family as the Prico™ process. The refrigerant fluid has the following composition:

- nitrogen: 4.67 mol%;
- methane: 29.17 mol%;
- ethane: 34.00 mol%;
- 15 – propane: 11.09 mol%;
- isobutane: 4.58 mol%;
- n-butane: 2.25 mol%;
- isopentane: 6.01 mol%;
- n-pentane: 8.23 mol%.

20 The single cycle may be cooled down according to the succession of steps (a) to (c) described above.

Example 2 – start-up example for a cooling unit according to the invention

This example is based on the cooling unit illustrated in Fig. 1.

25 One begins by carrying out cleaning of all the circuits with natural gas or « defrost gas », taken at the outlet of drum A6, the composition of which is the following:

- nitrogen: 4.4 mol%;
- methane: 87.8 mol%;
- ethane: 5.3 mol%;
- 30 – propane : 1.8 mol%;
- butane: 0.7 mol%.

Next, cycle B (pre-refrigeration circuit), which is an ethane/propane cycle, is cooled down to a temperature of about -65°C.

35 One then proceeds with cooling down cycle C (the refrigeration circuit corresponding here to a liquefaction and subcooling circuit), wherein the refrigerant fluid should have the following final composition:

- nitrogen: 7.5 mol%;
- methane: 42.5 mol%;

- ethane: 45 mol%;
- propane: 5 mol%.

To do this, the purge of the « defrost gas » is closed, and the components are then injected in the following order: ethane, propane, again natural gas (« defrost gas ») and finally nitrogen.

Table 1 below summarizes the change in the parameters of cycle C during its cooling down. Six successive instants during this cooling down are designated by t1 to t6. T1 designates the temperature at the cold end of exchanger 2. P1 represents the discharge pressure of compressor C7 in absolute bars. T2 represents the discharge temperature of compressor C7. %N₂ represents the nitrogen proportion in the circuit. %C₁ represents the proportion of methane in the circuit. %C₂ represents the proportion of ethane in the circuit. %C₃ represents the proportion of propane in the circuit. %C₄ represents the proportion of butane in the circuit. ΔT represents the maximum deviation of temperature in exchanger 2. Finally, as a comparison, ΔT' represents the maximum temperature deviation in exchanger 2 which would be obtained for a same temperature T1, if the prior art procedure was used consisting of filling the circuit with « defrost gas » before injecting ethane.

Table 1 – putting the refrigeration cycle into a cold state

	t1	t2	t3	t4	t5	t6
T1	-55°C	-75°C	-100°C	-120°C	-140°C	-155°C
P1	3 bar	9 bar	11.9 bar	12.6 bar	13,4 bar	56 bar
T2		139°C	157°C	160°C	163°C	
%N₂	4.4 %	3.1 %	2.5 %	2.5 %	2.4 %	7.5 %
%C₁	87.8 %	60.1 %	50.5 %	48.6 %	46.6 %	42.5 %
%C₂	5.3 %	35.1%	45.5 %	47.6 %	49.7 %	45 %
%C₃	1.8 %	1.3 %	1.1 %	1.0 %	1.0 %	5 %
%C₄	0.7 %	0.5 %	0.4 %	0.4 %	0.4 %	0.0 %
ΔT		18°C	23°C	21°C	23°C	12°C
ΔT'		58°C	60°C	61°C	60°C	12°C

Instant t1 corresponds to the beginning of the cooling down the cycle. The composition is that the « defrost gas » which was used for cleaning the loop. Compressor pressure P1 is very low on the one hand so as not to introduce too much initial methane, on the other hand because a too high pressure would be unnecessary for sweeping the equipment with the gas. Ethane is then added in order to reduce the temperature T1. As the defrosting phase is accomplished at low pressure, the mass inventory of the « defrost gas » is low and by adding ethane up to its total inventory it is possible to rapidly increase the average molar mass of the refrigerant fluid.

At instant t5, the temperature reaches -140°C and the ethane composition is larger than that in normal operation. A pressure of 13.4 bar (absolute) is then sufficient for condensing the refrigerant fluid whereas the compressor is capable in normal operation of providing 56.4 bars (absolute) with a gas of lower average molar mass for the same suction pressure.

It should be noted that if the cooling down was accomplished by means of the « defrost gas », the discharge temperature of compressor t2 may reach or even exceed 200-250°C because of the strong compression rate required for obtaining condensation of the gas.

The butane present in the loop is a remainder of the « defrost gas » and is gradually diluted as the ethane, propane and nitrogen inventory increases, until it is only present in a negligible amount.

At each of steps t2 to t5, the inventory in the circuit increases by adding ethane. Between t5 and t6, an ethane supplement is added in a first phase, and then in a second phase propane, again the natural gas (« defrost gas ») and nitrogen in order to reach the inventory of each component.

Figs. 2 and 3 illustrate the exchange diagrams in exchanger 2 at the t2 and t5 steps mentioned above, respectively. It can be seen that the temperature deviations do not exceed twenty degrees, i.e. are acceptable for all the cryogenic exchanger technologies, whereas they exceed 50°C with the prior art procedure, the maximum currently accepted by the designers being 30°C

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

The Claims defining the invention are as follows:

1. A method for starting up a natural gas liquefaction unit comprising a refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons, wherein the method successively comprises:
- 5 (a) the injection and purge of a cleaning gas into the refrigeration circuit;
(b) the injection of a first filling gas into the refrigeration circuit;
(c) the injection of a second filling gas into the refrigeration circuit;
the average molar mass of the first filling gas being greater than the average
10 molar mass of the second filling gas,
wherein the refrigeration circuit comprises a heat exchanger comprising a hot inlet and a cold inlet, and wherein the temperature of the refrigerant fluid at the cold inlet of the heat exchanger decreases by at least 30°C, preferably by at least 40°C, more particularly by at least 60°C, between the beginning and end of step
15 (b).
2. The method according to claim 1, wherein the first filling gas comprises at least 50 mol%, preferably at least 80 mol%, most preferably at least 90 mol%, ideally at least 95 mol%, of ethane.
- 20 3. The method according to claim 1 or 2, wherein the second filling gas preferably comprises at least 50 mol% of methane, most preferably at least 70 mol%, or even at least 80 mol%, of methane.
- 25 4. The method according to any one of claims 1 to 3, wherein the cleaning gas and/or the second filling gas are de-acidified and dried natural gas.
5. The method according to any one of claims 1 to 4, comprising, after step (a), and preferably after step (b), one or more steps of injecting additional filling gases
30 into the refrigeration circuit, each additional filling gas preferably comprising nitrogen, propane, isobutane, n-butane, isopentane, n-pentane, ethylene, propylene, or a mixture thereof.
- 35 6. The method according to any one of claims 1 to 5, wherein the first and the second filling gases provide at least 50%, preferably at least 60%, most preferably at least 70%, or even at least 80%, of the molecules of the refrigerant fluid which are present in the refrigeration circuit at the end of the start-up method.

7. The method according to any one of claims 1 to 6, wherein the refrigeration circuit comprises a Joule-Thompson expansion valve comprising an inlet and an outlet, and wherein the temperature difference of the refrigerant fluid between said inlet and said outlet is less than 40°C, preferably less than 30°C, ideally less than 25°C, throughout the method.
8. The method according to any one of claims 1 to 7, wherein the natural gas liquefaction unit further comprises a pre-refrigeration circuit and wherein the pre-refrigeration circuit is set to nominal operation before step (b).
9. The method according to any one of claims 1 to 8, wherein the natural gas liquefaction unit further comprises an additional refrigeration circuit.
10. The method according to claim 9, wherein the additional refrigeration circuit is a refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons, and wherein the method comprises, after step (c):
- (d) the injection of the first filling gas into the additional refrigeration circuit; and
 - (e) the injection of the second filling gas into the additional refrigeration circuit.
11. The method according to any one of claims 1 to 7, wherein said refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons is the only refrigeration circuit of the natural gas liquefaction unit.
12. A method for liquefying natural gas in a natural gas liquefaction unit comprising a refrigeration circuit containing a refrigerant fluid which comprises a mixture of hydrocarbons, wherein the method comprises:
- starting up the natural gas liquefaction unit, according to the method of any one of claims 1 to 11; and then
 - cooling and liquefying natural gas in said natural gas liquefaction unit.
13. A method for starting up a natural gas liquefaction unit substantially as hereinbefore described with reference to the accompanying Examples and Figures.

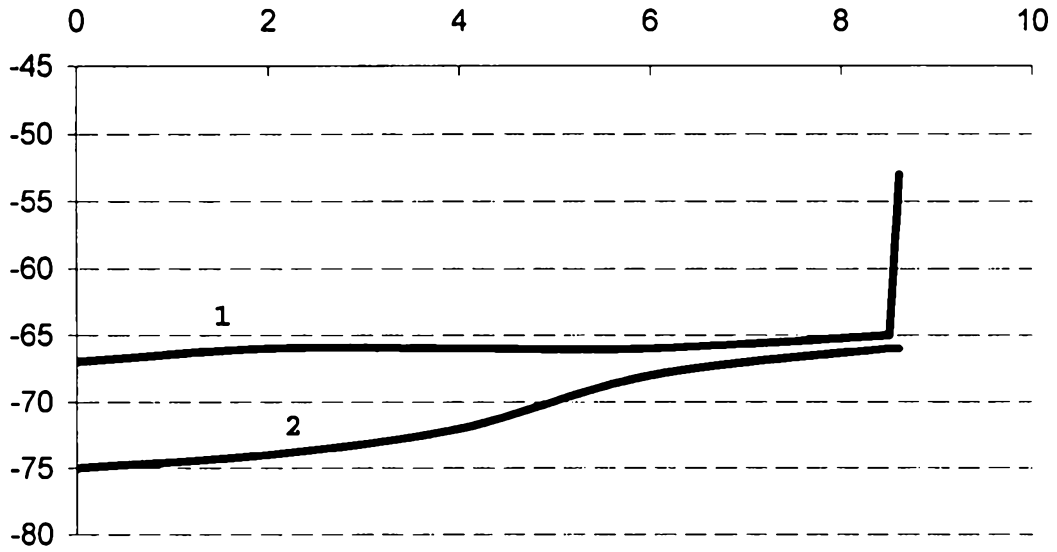


Figure 2

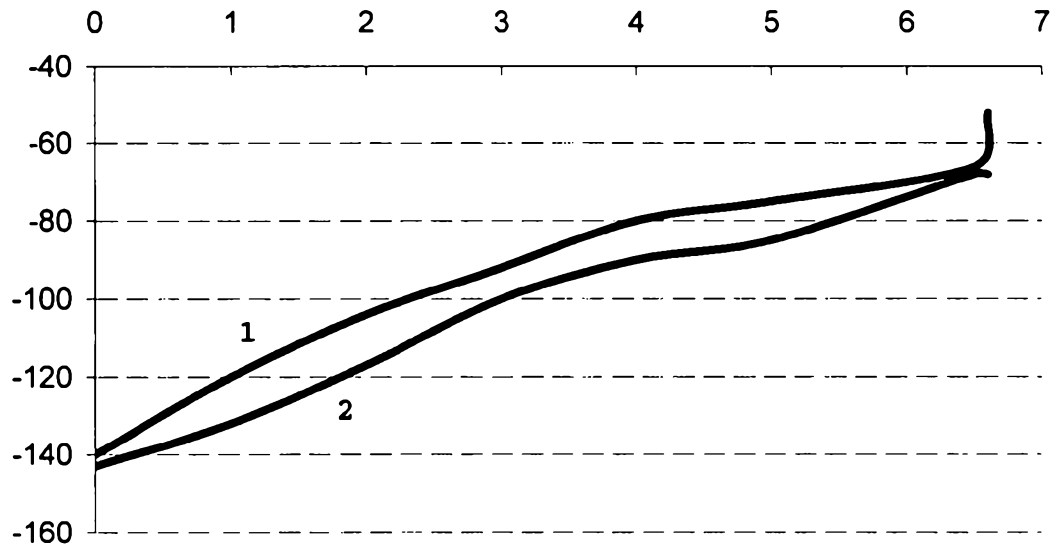


Figure 3