Description

Title: Method and apparatus for cooling hydrogen

The present invention relates to a method and to an apparatus for cooling hydrogen.

It is known to use to optimise a method for cooling hydrogen by recovering cold energy from the vaporisation of liquefied natural gas (LNG).

It is known to liquefy hydrogen in two steps:

- a first step of pre-cooling using a nitrogen cycle or a mixed refrigerants cycle followed by
- a second step of liquefying the cooled hydrogen with a cycle of hydrogen, helium or mixed refrigerants including rare gases.

The present invention proposes a solution for start-up of a method of which the first step of precooling the hydrogen is done using the cold energy of a flow of liquefied natural gas that is vaporised or vaporised natural gas, the vaporised natural gas being at a temperature lower than -50°C.

In this case, the liquefaction apparatus does not comprise an internal source for producing cold, at the moment of start-up.

In stable operation, the liquefied natural gas, for example, is heated, or even vaporised, against an intermediate fluid, which is cooled down to a temperature lower than -50°C, or even lower than -140°C. The heat exchanger used to heat the liquefied natural gas is typically a brazed aluminium plate and fin exchanger or a stainless steel exchanger or a printed circuit exchanger. During start-up of the method, the heat exchanger and the associated equipment has to be cooled from ambient temperature down to the temperature of stable operation. These elements are sensitive to rapid or excessive temperature drops and therefore require very particular attention in order to be cooled.

It is known to use a cycle to transfer the heat of vaporisation of the liquefied natural gas to the hydrogen that is cooled, this cycle comprising a compressor with an inlet temperature preferably lower than -90°C and optionally an expansion turbine. The cooling of such a compressor during start-up requires particular attention.

“Large scale hydrogen liquefaction in combination with LNG gasification” by Kuendig et al., 16th World Hydrogen Energy Conference 2006 describes a method according to the preamble of Claim 1.

According to one subject of the invention, a method for cooling hydrogen is provided, wherein

according to a first mode of operation

i) either liquefied natural gas or vaporised natural gas, the vaporised natural gas being at a temperature lower than -50°C, is heated by indirect heat exchange in a first heat exchanger with a flow of intermediate fluid at a pressure of between 3 and 70 bar abs that is cooled down to a temperature higher than or equal to -145°C

ii) the flow of intermediate fluid at a temperature higher than or equal to -145°C is cooled

a) by introducing it at this temperature into a second heat exchanger where it is cooled by indirect heat exchange and/or

b) by expansion in a turbine, optionally driving a compressor of the method, or a valve

iii) a flow of gaseous hydrogen is cooled in the second heat exchanger without condensing

iv) a gaseous flow derived from the intermediate fluid cooled in step a) and/or b) is heated in the second heat exchanger up to a temperature of between -90°C and -150°C, is withdrawn from the exchanger at this temperature and compressed in a compressor with an inlet temperature of between -90°C and -150°C and at least one part of the compressed intermediate fluid is cooled first in the first heat exchanger and then heated from a temperature of at most -110°C and

v) the at least one part of the heated intermediate fluid constitutes the flow of intermediate fluid of step i) and

characterized in that the compressed intermediate fluid cooled in the first heat exchanger is heated in the second heat exchanger and in that

during a start-up mode

i) the flow of hydrogen is not sent to the second exchanger,

ii) supercritical natural gas or a gas at less than -100°C is sent to the first exchanger so as to cool it and exchanges heat there with a flow of intermediate fluid of a cycle at a pressure of between 3 and 70 bar abs that is cooled,

iii) the flow of intermediate fluid cooled in the first exchanger is sent directly to the inlet of the compressor that compresses it with a compression rate less than that of the first mode, the molar flow rate of the intermediate fluid being less than 80% of the molar flow rate of intermediate fluid sent to the compressor during the first mode and

iv) the intermediate fluid compressed in the compressor is sent back to the first exchanger as cycle fluid.

According to other optional aspects:

- the intermediate fluid contains more than 50 mol% nitrogen, preferably at least 90 mol% nitrogen or even at least 99 mol% nitrogen.
- during start-up the supercritical natural gas is pseudo-vaporised in the first heat exchanger and preferably heated there up to a temperature higher than 0°C.
- during start-up, the gas at less than -100°C is heated in the first heat exchanger and the heated gas has the same composition as the intermediate fluid
- the gas heated in the first heat exchanger is sent to the cycle so as to supply it.
- during start-up, if the inlet or outlet temperature of the compressor passes below a threshold, the flow of intermediate fluid cooled in the first exchanger is sent to be expanded in the turbine and the expanded fluid is sent back to be heated in the second exchanger and then to the compressor.
- the turbine is coupled to a booster that, during start-up, boosts fluid compressed in the compressor only if the turbine expands intermediate fluid.
- the compressor comprises at least two stages and the intermediate fluid is not cooled between the stages of the compressor.
- during the first mode, compressed intermediate fluid is cooled first in the first heat exchanger, is heated in the second heat exchanger and is cooled again in the first heat exchanger before being sent to the turbine and, during start-up, compressed intermediate fluid is cooled first in the first heat exchanger, is heated outside the second heat exchanger optionally by a heater and is cooled again in the first heat exchanger.

According to another subject of the invention, an apparatus for cooling hydrogen is provided, comprising a first heat exchanger, means for sending either liquefied natural gas or vaporised natural gas, the vaporised natural gas being at a temperature lower than -50°C, to be heated by indirect heat exchange in the first heat exchanger with a flow of intermediate fluid at a pressure of between 3 and 70 bar abs that is cooled down to a temperature higher than or equal to -145°C, a second heat exchanger, means for sending the flow of intermediate fluid at a temperature higher than or equal to -145°C to be cooled by introducing it at this temperature into a second heat exchanger where it is cooled by indirect heat exchange and/or by expansion in a turbine, optionally driving a compressor of the method, or a valve,

means for sending a flow of gaseous hydrogen to be cooled in the second heat exchanger without condensing, means for sending a gaseous flow derived from the cooled intermediate fluid to be heated in the second heat exchanger up to a temperature of between -90°C and -150°C, means for withdrawing the gaseous flow from the second exchanger at this temperature, a compressor with an inlet temperature of between -90°C and -150°C, means for sending the withdrawn gaseous flow to the compressor with an inlet temperature of between -90°C and -150°C, means for sending at least one part of the compressed intermediate fluid to be cooled first in the first heat exchanger and then heated from a temperature of at most -110°C, the at least one part of the heated intermediate fluid constituting the flow of intermediate fluid of step i)
characterized in that it comprises means for sending the compressed intermediate fluid cooled in the first heat exchanger to be heated in the second heat exchanger.

According to other optional aspects of the invention:

- the turbine is coupled to a booster,
- the compressor comprises at least two stages, without means for cooling the intermediate fluid between the stages of the compressor.

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The use of an intermediate fluid makes it possible to better regulate the integration by differentiating the hydrogen and LNG networks.
The vaporisation of the LNG is done in a single exchanger and the intermediate fluids distributes the cold towards the various consumers.
The intermediate cycle, by virtue of an expansion step, makes it possible to produce a cold fluid with a lower temperature than the LNG.
[FIG.1] illustrates a cooling, or even liquefaction, method according to the invention.
[FIG.2] illustrates another cooling, or even liquefaction, method according to the invention.
In stable operation, the method for cooling hydrogen operates in the following manner. A dedicated heat exchanger E1 serves to recover the cold energy from the liquefied natural gas 1 at -150°C using an intermediate fluid that is cooled by the liquid 1 in the exchanger E1. The exchanger E1 may be a brazed aluminium plate

and fin exchanger or a stainless steel exchanger or a printed circuit exchanger. Otherwise, the exchanger E1 may be a shell and tube exchanger.

The liquid 1 is heated, for example up to 15°C, and optionally vaporised so as to cool the fluid 5 down to a temperature lower than -50°C, preferably lower than -120°C.

The fluid 5 is cooled in the exchanger E1 down to a temperature higher than or equal to -145°C. In the example it is cooled down to -140°C. The heat exchanger may be an aluminium or stainless steel plate and fin exchanger or a shell and tube exchanger.

The fluid 1 enters at the cold end of the exchanger E1 and leaves at the hot end as fluid 3.

In the example, the fluid 5 is nitrogen. It may, for example, be natural gas or methane, or may have another suitable composition. Preferably, the fluid 5 is inert. The fluid 5 is preferably at a pressure of between 3 and 70 bar abs.

The nitrogen 13 leaves the exchanger E2 at a temperature of between -90°C and -150°C, for example at -120°C, and is compressed in a first compressor C, for example a centrifugal compressor, to approximately 20 bar. Then the nitrogen at 20 bar is cooled R and compressed in another compressor C1 to a pressure higher than 20 bar. Then the nitrogen at more than 20 bar is optionally divided into two parts 15, 17, the part 17 not necessarily being present. The part 17 may be cooled partially in the exchanger E1 and then is sent to an element to be cooled 31. Thus the heated part 19 is sent to the hot end of the exchanger E1. The part 15 added to 19 forms a flow 21 that is sent at 20°C to the hot end of the exchanger E1 and is cooled there down to a temperature of lower than 90°C, for example -140°C, forming a gas 27 that is sent to the exchanger E2 at a temperature of -140°C. The gas 27 is heated in the exchanger E2 up to 20°C (forming the flow 6) then the flow 6 is cooled against the LNG in the exchanger E1 so as to form the gas 5. In this example, the gas 5 is not cooled in the exchanger E1 but only in the turbine E. Thus the gas 5 enters the turbine E at the temperature at which it leaves the heat exchanger E1. The expanded fluid 7 at 1.5 bar in the turbine T is two-phase and is sent to a phase separator where it forms a liquid 9 and a gas 11. The liquid is vaporised in a heat exchanger E3 and joins the gas 11 so as to be heated in the exchanger E2 constituting the flow 13 to be sent to the cold compressor C. All the gas 13 is compressed in the cold compressor 1 and then in a booster C1 coupled to the turbine E. It is the gas compressed in the booster C1 that is sent to the exchanger E1 so as to recover cold from the LNG 1.

As a variant, the gas 5 coming from the cold end of the exchanger E1 may first pass into the exchanger E1 so as to be cooled and then be expanded in a turbine T having an inlet temperature lower than -100°C, for example -120°C.

Thus the nitrogen, or another fluid, for example helium or a mixed refrigerant, circulates in a closed cycle, taking cold energy from the LNG.

The gaseous hydrogen 23 at ambient temperature, for example 20°C, enters at the hot end of the heat exchanger E2 that it passes through from one end to the other so as to be cooled down to a temperature of lower than -150°C, for example -180°C. It is then cooled in heat exchanger E3 against the liquid of the phase separator so as to form gaseous hydrogen 25 at -190°C.

The hydrogen 25 is then cooled and liquefied in another heat exchanger in a known manner. A cycle of hydrogen, helium or mixed refrigerants including rare gases provides the necessary cold energy.

Thus the LNG provides at least a part of the cold energy necessary for the precooling of the gaseous hydrogen down to -190°C. This fraction may be at least 50%, at least 75%, or at least 99% of the cold energy necessary for the cooling of the gaseous hydrogen down to -190°C. The LNG may even provide all the necessary cold energy apart from that coming from the turbine T.

The method may also provide cold to another element 31, cooled by the cycle. In the figure, it can be seen that a part 17 of the gas compressed in the compressors C, C1 is cooled in the heat exchanger down to an intermediate temperature, in this case -50°C, is withdrawn from the exchanger in a central zone of the heat exchanger and serves to cool the element 31 by being itself heated to form the gas 19 that joins the flow 15 compressed in the compressor C so as to form the flow 21 that enters the exchanger E1 at 20°C. As the pressure drops for the flow 18, 19 are limited, a small expansion of the flow 15 in a valve will be sufficient to allow the flows 15, 19 to mix.

The element 31 may for example be a liquefier for another gas or an apparatus for separation by distillation and/or partial condensation at a temperature lower than 0°C, for example a carbon dioxide liquefier.

If the fraction 17 is present but the element 31 is not in operation, a heater, for example an electric heater or a heat exchanger heated with hot water, will serve to heat the fraction 17 so as to form the flow 19.

During start-up of the apparatus, the hydrogen 23 is not sent to the exchanger E2 that has to be cooled beforehand. The cycle compressor C is started up with an inlet

temperature that is ambient temperature at a reduced load, typically between 60 and 80% of the nominal molar flow rate. The compression rate is also limited in order to limit the outlet temperature of the compressor C to a reasonable value, typically less than 150°C. The compressor C may comprise no inter-stage cooling, with only a final cooler R upstream of the compressor C in order to reduce the cost of the machine and to limit the risk of the water in the intermediate water coolers freezing, which coolers are bypassed in stable operation where the temperature of the gas being compressed is lower than 0°C, the compression rate is reduced considerably so as to limit the temperature at the outlet of the compressor C1 upstream of the final cooler. For start-up, a variable frequency drive could vary the speed of the motor of the compressor C and thus the temperature of the final stage of C and the compression rate.

Before start-up of the turbine E, the compressor C1 does not compress the nitrogen that passes through a bypass duct 13A.

The nitrogen compressed in the compressor C only is sent to the first heat exchanger E1 that is not supplied at start-up with the liquefied natural gas 1 but with liquid nitrogen coming from a store S that is vaporised by a vaporiser V so as to form gaseous nitrogen 2 at -180°C. The use of vaporised cold gas rather than a liquid makes it possible to protect the equipment from excessively sudden cooling and from thermal stresses. The gaseous nitrogen is heated in the exchanger E1 and is recovered at the cold end or sent into the air.

As a variant, as illustrated in [FIG. 2], the exchanger E1 may be cooled by means of the sending of supercritical liquefied natural gas. This fluid has the advantage of reduced enthalpy of vaporisation compared with non-supercritical LNG. For this, the liquefied natural gas 1 may be heated in a heater H in order to regulate its temperature at the inlet of the exchanger E1.

In the case of the two figures, the vaporised liquid other than the natural gas used for start-up (typically nitrogen) may be sent into the atmosphere or recovered at 15°C for example so as to serve in the cycle for cooling the intermediate fluid (compressor C, C1, turbine T) to replace leaks. The line for interconnection with the vaporised start-up liquid and the cycle may need to be well isolated so as to completely separate the LNG vaporisation line and the cooling cycle during normal operation (typically by removing the connection spool).

The cooling cycle (compressor C, C1, turbine T) at the outlet of the exchanger E1 will be cooled slowly down to the operating temperature. As long as the temperature of the outlet of the exchanger E1 is above the operating temperature, the gas 5 will not be sent either to the turbine or to the exchanger E2 but will pass through a duct 5A directly to the inlet of the compressor C in order to cool it slowly.

During the drop in the inlet temperature of the compressor C, the compression rate of the compressor C will increase since its inlet temperature will drop.

A temporary heater W (typically an exchanger supplied with water) may be used only during start-up to replace the introduction of heat from the exchanger E2. This heater W may be bypassed in stable operation of the method. It heats the flow 27 of nitrogen sent via the duct 27A, preventing the flow 27 from passing into the exchanger E2.

Once the compressor C has been cooled and is in operation at reduced load, typically between 60 and 80% of the nominal molar flow rate, the cooling of the hydrogen precooling system starts. First, the turbine E is bypassed by the line 5E so that the gas 5 passes directly into the phase separator (that does not yet separate phases, since the gas 5 has not been condensed). Then, the turbine and its associated compressor C1 are started up, the gas compressed in the compressor C no longer passing through the bypass line 13A and being compressed in the compressor C1.

The main advantage of this method is that it uses existing equipment with some minimal additions to cool, without safety problems, the apparatus for cooling the hydrogen, with regulated start-up of the sensitive equipment.

Claims

1. Method for cooling hydrogen, wherein

according to a first mode of operation:

i) either liquefied natural gas (1, 2) or vaporised natural gas, the vaporised natural gas being at a temperature lower than -50°C, is heated by indirect heat exchange in a first heat exchanger (E1) with a flow of intermediate fluid (5) at a pressure of between 3 and 70 bar abs that is cooled down to a temperature higher than or equal to -145°C

ii) the flow of intermediate fluid at a temperature higher than or equal to -145°C is cooled

a) by introducing it at this temperature into a second heat exchanger (E2) where it is cooled by indirect heat exchange and/or

b) by expansion in a turbine (E), optionally driving a compressor of the method (C, C1), or a valve

iii) a flow of gaseous hydrogen (23) is cooled in the second heat exchanger without condensing

iv) a gaseous flow (13) derived from the intermediate fluid cooled in step a) and/or b) is heated in the second heat exchanger (E2) up to a temperature of between -90°C and -150°C, is withdrawn from the exchanger at this temperature and compressed in a compressor (C, C1) with an inlet temperature of between -90°C and -150°C and at least one part of the compressed intermediate fluid (15, 17) is cooled first in the first heat exchanger and then heated from a temperature of at most -110°C and

v) the at least one part of the heated intermediate fluid constitutes the flow of intermediate fluid of step i)

characterized in that the compressed intermediate fluid cooled in the first heat exchanger is heated in the second heat exchanger and in that

and during a start-up mode

i) the flow of hydrogen is not sent to the second exchanger,

ii) supercritical natural gas (1, 2) or a gas at less than -100°C is sent to the first exchanger so as to cool it and exchanges heat there with a flow of intermediate fluid (5) of a cycle at a pressure of between 3 and 70 bar abs that is cooled

iii) the flow of intermediate fluid (5) cooled in the first exchanger is sent directly to the inlet of the compressor (C, C1) that compresses it with a compression rate less than

that of the first mode, the molar flow rate of the intermediate fluid (13) being less than 80% of the molar flow rate of intermediate fluid sent to the compressor during the first mode and

iv) the intermediate fluid (15, 17) compressed in the compressor is sent back to the first exchanger as cycle fluid.

2. Method according to one of the preceding claims, wherein the intermediate fluid (5) contains more than 50 mol% nitrogen, preferably at least 90 mol% nitrogen or even at least 99 mol% nitrogen.

3. Method according to either of the preceding claims, wherein during start-up the supercritical natural gas (1, 2) is pseudo-vaporised in the first heat exchanger (E1) and preferably heated there up to a temperature higher than 0°C.

4. Method according to either of the preceding Claims 1 and 2, wherein during start-up, the gas at less than -100°C is heated in the first heat exchanger (E1) and the heated gas has the same composition as the intermediate fluid (5).

5. Method according to Claim 4, wherein the gas (3) heated in the first heat exchanger (E1) is sent to the cycle so as to supply it.

6. Method according to one of the preceding claims, wherein during start-up, if the inlet or outlet temperature of the compressor (C, C1) passes below a threshold, the flow of intermediate fluid cooled in the first exchanger is sent to be expanded in the turbine (E) and the expanded fluid is sent back to be heated in the second exchanger (E2) and then to the compressor.

7. Method according to Claim 6, wherein the turbine (E) is coupled to a booster (C1) that, during start-up, boosts fluid compressed in the compressor (C) only if the turbine expands intermediate fluid.

8. Method according to one of the preceding claims, wherein the compressor (C, C1) comprises at least two stages and the intermediate fluid is not cooled between the stages of the compressor.

9. Method according to one of the preceding claims, wherein, during the first mode, compressed intermediate fluid (6) is cooled again in the first heat exchanger (E1) before being sent to the turbine (E) and, during start-up, compressed intermediate fluid is cooled first in the first heat exchanger, is heated outside the second heat exchanger optionally by a heater (W) and is cooled again in the first heat exchanger.

10. Apparatus for cooling hydrogen, comprising a first heat exchanger (E1), means for sending either liquefied natural gas (1, 2) or vaporised natural gas, the vaporised natural gas being at a temperature lower than -50°C, to be heated by indirect heat exchange in the first heat exchanger (E1) with a flow of intermediate fluid (5) at a pressure of between 3 and 70 bar abs that is cooled down to a temperature higher than or equal to -145°C, a second heat exchanger (E2), means for sending the flow of intermediate fluid at a temperature higher than or equal to -145°C to be cooled by introducing it at this temperature into a second heat exchanger (E2) where it is cooled by indirect heat exchange and/or by expansion in a turbine (E), optionally driving a compressor of the method (C, C1), or a valve, means for sending a flow of gaseous hydrogen (23) to be cooled in the second heat exchanger without condensing, means for sending a gaseous flow (13) derived from the cooled intermediate fluid to be heated in the second heat exchanger (E2) up to a temperature of between -90°C and -150°C, means for withdrawing the gaseous flow from the second exchanger at this temperature, a compressor (C, C1) with an inlet temperature of between -90°C and -150°C, means for sending the withdrawn gaseous flow to the compressor (C, C1) with an inlet temperature of between -90°C and -150°C, means for sending at least one part of the compressed intermediate fluid (15, 17) to be cooled first in the first heat exchanger and then heated from a temperature of at most -110°C, the at least one part of the heated intermediate fluid constituting the flow of intermediate fluid of step i)

characterized in that it comprises means for sending the compressed intermediate fluid cooled in the first heat exchanger to be heated in the second heat exchanger.

11. Apparatus according to Claim 10, wherein the turbine (E) is coupled to a booster (C1).

12. Apparatus according to either of the preceding Claims 10 and 11, wherein the compressor (C, C1) comprises at least two stages, without means for cooling the intermediate fluid between the stages of the compressor.