A PROCESS FOR HANDLING A HYDROGEN BOG STREAM

Field of the Invention

The present invention relates to a process for handling a hydrogen BOG (boil-off gas) stream.

Background of the Invention

Hydrogen is seen as one of the most promising energy carriers for a decarbonized energy system. Efficient transport and storage of liquid hydrogen (LH_2) are seen as critical to its large-scale adoption.

One of the main challenges of the storage of liquid hydrogen is the handling of hydrogen boil-off losses due to the requirement to cool down, filling of storage tanks, heat ingress, the need to depressurize storage tanks, etc.

Some boil-off gas will be formed continuously, at a stable flow rate, such as during system holding mode due to heat ingress. Other boil-off gas will be formed intermittently. Typically, these latter, intermittent boil-off gas flows will be of short duration (in the order of hours), have a relatively high-peak flow (instantaneous flows of 2 to 10 times the average daily processing rates) and a low frequency (e.g. once to ten times a month).

Furthermore, some boil-off gas may have a temperature that is significantly higher than the hydrogen ambient pressure boiling point of -253 °C (20 K). In this respect, the thesis by A. Krenn on "*The safe removal of frozen air from the annulus of a liquid hydrogen storage tank*" (available through https://stars.library.ucf.edu/etd/1382) depicts in Figure

6 modelling results of the temperature stratification of hydrogen gas in a steady-state, 50 % filled, LH_2 tank. Hydrogen boil-off gas temperatures of above -34.65 °C (238.5 K) are predicted.

The above 'intermittent' or 'variable' nature of certain hydrogen boil-off gas flows makes it difficult for e.g. mechanical equipment to deal with. If no adequate solution is available to handle these intermittent BOG flows, the intermittent hydrogen BOG is vented. It goes without saying that this venting of hydrogen BOG is economically and environmentally undesirable.

The article by Notardonato et al. "*Final test results for the ground operations demonstration unit for liquid hydrogen*" in Cryogenics 88 (2017) 147-155 describes a LH_2 system using IRAS (Integrated Refrigeration and Storage) technology aiming at ZBO (zero boil-off) operations, i.e. avoiding the occurrence of hydrogen BOG.

A problem of the above IRAS technology is that it is costly and complicated. Another problem with the IRAS technology is, that although it will reduce boil-off, for example on cargo transfer operations, it does not completely eliminate boil-off generation and hence boil-off handling will still be required. Further, the IRAS technology has not been designed to re-process and recondense intermittent boil-off gas flows.

Several processes for handling hydrogen BOG (instead of venting) have recently been proposed in the art.

US 2023/0009727 A1 describes a method for the liquefaction of hydrogen. The method includes the steps of: precooling a hydrogen feed stream in a precooling cold box having a heat exchanger disposed therein to form a cooled hydrogen stream, wherein the heat exchanger is

configured to cool down the feed stream within the precooling cold box by indirect heat exchange between the hydrogen feed stream and a precooling refrigerant; and withdrawing the cooled hydrogen stream from the precooling cold box; introducing the cooled hydrogen stream to a plurality of liquefaction cold boxes, wherein the cooled hydrogen stream liquefies within the plurality of liquefaction cold boxes by indirect heat exchange against a liquefaction refrigerant to form a product hydrogen stream in each of the plurality of liquefaction cold boxes.

Paragraph [0005] of US 2023/0009727 A1 states that: "*It is known in the art that the largest equipment within the cold boxes are the heat exchangers*". US 2023/0009727 A1 thereby makes an explicit distinction between the heat exchanger equipment and the cold boxes in which the heat exchanger equipment resides, both forming part of the liquefaction system.

In US 2023/0009727 A1, the person skilled in the art would readily understand that the dashed rectangles 10 and 5 in Figure 1 and 10, 20 and 25 in Figures 3 and 4 indicate which process equipment is enclosed in the precooling or liquefaction cold boxes.

As a mere example, Figure 3 and paragraph [0076] of US 2023/0009727 A1 disclose rewarming boil-off gas streams 42,43 that are withdrawn from hydrogen liquid storage tank 40 in one or both liquefaction zones before being combined and rewarmed more in the precooling zone 10. A simplified version of Figure 3 of US 2023/0009727 A1 is shown herein as Figure 1.

A problem of the afore-mentioned line-up in US 2023/0009727 A1 is that, in particular with the occurrence of variable flows and/or variable temperatures

of hydrogen BOG, this may result in mechanical stresses (and failures) in the heat exchanger equipment. A further problem of this line-up is that, in particular with the occurrence of high flows of hydrogen BOG, the flow capacity of the heat exchanger equipment may be exceeded.

US 3380809 A is directed to a process for liquefaction and conversion of hydrogen. Specifically, US 3380809 A provides a process for producing liquid hydrogen of high para composition which comprises:

- passing compressed hydrogen feed in countercurrent heat interchange with relatively cold fluid and catalytically converting ortho-hydrogen to para-hydrogen to provide high para composition hydrogen feed at a relatively low temperature,
- expanding high para composition hydrogen feed to a lower pressure effect partial liquefaction of the high para composition hydrogen feed,
- separating high para composition liquid hydrogen from high para composition unliquefied hydrogen,
- catalytically treating high para composition liquid - hydrogen to increase further the para composition of the liquefied hydrogen,
- warming high para composition unliquefied hydrogen and compressing warm high para composition hydrogen to a relatively high pressure,
- passing compressed high para composition unliquefied hydrogen in countercurrent heat interchange with relatively cold fluid to cool compressed high para composition unliquefied hydrogen to a low temperature without catalytic conversion of ortho-hydrogen,
- expanding cool high para composition unliquefied hydrogen, and

- catalytically treating expanded high para composition hydrogen to increase further its para composition.

Figures 1A-1D in US 3380809 A show a complex arrangement of equipment used in the liquefaction and refrigeration cycles. It is apparent that arrangement employed in US 3380809 A involves recirculating of streams and results in intimate mixing (i.e. blending) of various streams, including hydrogen feed stream, hydrogen refrigerant stream and hydrogen BOG streams, in the system. In particular, it is apparent that hydrogen BOG streams 200 and 201 therein are routed through the so-called “hydrogen refrigeration and recycle arrangement” in the system. Hydrogen (e.g., refrigerant/BOG) streams in this arrangement are later cycled back through the system such that there is further intimate mixing of such streams with hydrogen feed stream at various points in the system.

For example, where compressed heated hydrogen BOG stream 151 mixes with intermediate pressure hydrogen stream 184, which functions as a refrigerant in this arrangement, at the inlet of compressor 152. US 3380809 A clarifies at column 7, lines 67-70 that this flow of intermediate pressure hydrogen (181/182/183/184) “*through the shell side of the heat exchange devices 47 and 58 cools the hydrogen feed gas flowing through the passageways 46, 51, 55, 57, 61, 65, and 69*”.

By way of another example, where the combined BOG and intermediate pressure hydrogen streams 151 and 184 are compressed in compressor 152, cooled in heat exchangers 158 and 178 and liquefied upon expansion through valve 179 to yield a liquefied BOG-refrigerant stream 180 that mixes with the hydrogen feed gas in the conduit 71, upstream of the expansion valve 72.

By way of another example, where the combined BOG and intermediate pressure hydrogen streams 151 and 184 are compressed in compressor 152, cooled in heat exchangers 158, 47 and 58 and liquefied upon expansion through valve 169 to yield a liquefied BOG-refrigerant stream 170 that mixes with the hydrogen feed gas in the conduit 71, downstream of the expansion valve 169.

The skilled person will appreciate that, in view of the complex routing and recirculation arrangement described in US 3380809 A, intimate mixing of the various hydrogen feed, refrigerant and BOG streams would require careful balancing of the system. At column 8, lines 52-64, US 3380809 A speaks of reaching "*equilibrium conditions*", which is the operational state when the (combined) mass of certain streams "corresponds substantially" with the (combined) mass of certain other streams. Said system would encounter operating issues when having to cope with large fluctuations in flows and/or temperatures of hydrogen BOG. Such variability would result in challenges and mechanical stresses (and failures) in the arrangement of Figures 1A-1D. Such an arrangement would also struggle to cope with the occurrence of high flows of hydrogen BOG, such that the flow capacities of the multiple heat exchangers, conduits, or phase separators in the arrangement may be exceeded.

As a further example, WO 2023/046889 A1 discloses a hydrogen BOG recovery method wherein hydrogen BOG ('BOG1') originating from a hydrogen transport truck (i.e., relative small volume of hydrogen BOG) is handled "based on measurements of the pressure of the BOG" (see page 1, lines 19-21 and claim 1).

As WO 2023/046889 A1 focusses on relatively small hydrogen BOG volumes (originating from a hydrogen transport truck during truck loading/filling mode) it will not allow handling of larger hydrogen BOG volumes. Furthermore, WO 2023/046889 A1 discloses on page 1, lines 24-32 that the recovery of BOG can be maximized using hydrogen molecules in 3 different ways (including sending BOG to or upstream of the liquefiers and valorizing cold BOG directly in the liquefier). In case cold BOG is directly sent to the liquefier, the same shortcomings as in US 2023/0009727 A1 are encountered. In case boil-off hydrogen is sent to upstream of the liquefier(s), it is proposed to send "*specifically at compression trains inlet*" (see page 1, lines 29/30). As shown in the Figures, in that case a 'BOG heater' is used. In this respect it is noted that page 6, lines 23-24 specify that "*The BOG heater typically uses an external fluid, such as steam or water to warm the BOG.*". In this case no valorization of the cold BOG is achieved. Further, in this case any leakage between the cold fluid and warm fluid inside this BOG heater will lead to immediate water ice formation and plugging.

AU 2013/264212 A1 (also published as WO 2013/175906 A1) discloses (see e.g. [0011]) introducing boil-off gas which is generated in a primary LH_2 reservoir (for example a LH_2 vessel of a LH_2 transporting ship) in a secondary LH_2 reservoir so that at least a part of the BOG is liquefied by cryogenic heat energy of the (subcooled) LH_2 in the secondary LH_2 reservoir. A problem of this set-up is that this would require a large tank to be able to reliquefy hydrogen BOG, in particular in case of intermittent high-peak flows. Also, it would require maintaining a filled (and subcooled) LH_2 tank, also when

waiting for a next amount of hydrogen BOG to be reliquefied. The maintaining of such a filled LH_2 tank in waiting modus is inefficient, as hydrogen BOG will inherently be formed whilst in waiting modus. Further, in case the hydrogen BOG that is fed to the secondary tank would be of a lower quality (e.g. contaminated) this would also contaminate the content of the large secondary LH_2 vessel.

It is an object of the present invention to solve, minimize or at least reduce one or more of the above problems associated with the handling of hydrogen boil-off gas, in particular in case of variable, high amounts of hydrogen BOG such as occur during filling of larger hydrogen storage tanks.

It is another object of the present invention to provide a process for handling hydrogen BOG streams having varying or relatively high temperature.

It is a further object of the present invention to provide a process for handling a hydrogen BOG stream which is not dependent on measurement of hydrogen BOG pressure.

It is an even further object of the present invention to provide an alternative process for handling hydrogen BOG.

Summary of the Invention

One or more of the above or other objects may be achieved according to the present invention by providing a process for handling a hydrogen BOG (boil-off gas) stream, the process at least comprising the steps of:

(a) providing a hydrogen feed stream to be liquefied;

(b) cooling the hydrogen feed stream provided in step (a) in a liquefaction unit comprising a precooling cold box and a liquefaction cold box, using at least a first

refrigerant thereby obtaining an at least partly liquefied hydrogen stream, wherein the first refrigerant is, after leaving the liquefaction unit, compressed in a compressor to obtain a compressed first refrigerant and cooled in an external heat exchanger before being returned to the liquefaction unit;

(c) providing a hydrogen BOG stream;

(d) heating the hydrogen BOG stream provided in step (c) in the external heat exchanger against the compressed first refrigerant, thereby obtaining a heated hydrogen BOG stream;

(e) compressing the heated hydrogen BOG stream, thereby obtaining a compressed heated hydrogen BOG stream; and

(f) combining the compressed heated hydrogen BOG stream obtained in step (d) with the hydrogen feed stream provided in step (a); and

wherein the first refrigerant is in a closed refrigerant loop comprising the external heat exchanger, the compressor and the liquefaction unit.

The present invention further provides an apparatus suitable for performing the process for handling a hydrogen BOG (boil-off gas) stream, the apparatus at least comprising:

- a liquefaction unit comprising a precooling cold box and a liquefaction cold box, for cooling a hydrogen feed stream to be liquefied, using at least a first refrigerant, to obtain an at least partly liquefied hydrogen stream;
- a compressor for compressing the first refrigerant after the first refrigerant has left the liquefaction unit;

- an external heat exchanger for cooling the first refrigerant after the first refrigerant has left the compressor;

- one or more storage tanks that can be filled with liquefied hydrogen and can provide a hydrogen BOG stream;

wherein in the external heat exchanger, the hydrogen BOG stream can be heated against the first refrigerant, thereby obtaining a heated hydrogen BOG stream;

- a compressor for compressing the heated hydrogen BOG stream, thereby obtaining a compressed heated hydrogen BOG stream; and

- a joint for combining the compressed heated hydrogen BOG stream with the hydrogen feed stream,

wherein the first refrigerant is in a closed refrigerant loop comprising the external heat exchanger, the compressor and the liquefaction unit.

Brief Description of the Figures

Figure 1 is a simplified version of Figure 3 in US 2023/0009727 A1.

Figure 2 is a flow scheme of a (high level) first embodiment of the process for handling hydrogen BOG according to the present invention;

Figure 3 is a flow scheme of a second embodiment of the process for handling hydrogen BOG according to the present invention;

Figure 4 is a flow scheme of a third embodiment of the process for handling hydrogen BOG according to the present invention;

Figure 5 is a flow scheme of a fourth embodiment of the process for handling hydrogen BOG according to the present invention; and

Figure 6 is a flow scheme of a fifth embodiment of the process for handling hydrogen BOG according to the present invention.

While the present disclosure is susceptible to various modifications and alternative forms, specific embodiments have been shown in the figures and are herein described in more detail.

It should be understood, however, that the description of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, this disclosure is to cover all modifications and equivalents as illustrated, in part, by the appended claims.

Detailed Description of the Invention

It has surprisingly been found according to the present invention that by heating the hydrogen BOG stream in the external heat exchanger (i.e. external to the liquefaction unit) against the compressed first refrigerant, which first refrigerant is in a closed refrigerant loop, the handling of hydrogen BOG can be achieved in a simple way.

It is an important advantage of the process according to the present invention that intermittent or variable amounts of hydrogen BOG can be handled, without severe implications on, e.g., the heat exchanger equipment inside the liquefaction unit (which would occur in case large amounts of hydrogen BOG would directly be sent to the liquefaction unit).

A further advantage of the process according to the present invention is that by using an internal fluid to heat the hydrogen BOG (instead of the 'external fluid' (such as steam or water) as used in WO 2023/046889 A1)

valorization of cold BOG can be achieved resulting in a higher energy efficiency of the liquefaction unit.

An even further advantage of the process according to the present invention is that a wide range of BOG temperatures and changes of BOG temperatures can be handled, without severe implications on, e.g., the heat exchanger equipment inside the precooling and/or the liquefaction cold box.

In step (a) of the process according to the present invention, a hydrogen feed stream to be liquefied is provided.

Although the hydrogen feed stream provided in step (a) is not particularly limited, it typically has a high hydrogen content and is low in impurities (which would otherwise freeze in the conduits). Preferably, the hydrogen feed stream provided in step (a) comprises at least 99.0 wt.% hydrogen, preferably at least 99.8 wt.%, more preferably at least 99.9 wt.%.

Preferably, the hydrogen feed stream provided in step (a) has a pressure in the range of 15-80 bara, preferably below 50 bara, more preferably below 35 bara.

Generally, the hydrogen feed stream provided in step (a) will have a temperature of -40 to 55 °C (233 to 328 K), preferably in the range of from -20 to 55 °C (253 to 328 K), more preferably in the range of from -10 to 40 °C (263 to 313 K).

In step (b) of the process according to the present invention, the hydrogen feed stream provided in step (a) is cooled in a liquefaction unit using at least a first refrigerant thereby obtaining an at least partly liquefied hydrogen stream, wherein the first refrigerant is, after leaving the liquefaction unit, compressed in a compressor to obtain a compressed first refrigerant and

cooled in an external heat exchanger before being returned to the liquefaction unit.

As mentioned hereinbefore, the first refrigerant is in a closed refrigerant loop comprising the external heat exchanger, the compressor and the liquefaction unit. As stated hereinbefore, the liquefaction unit comprises a precooling cold box and a liquefaction cold box. The skilled person will understand that the liquefaction unit (and the precooling cold box and liquefaction cold box therein) may further comprise additional equipment therein, including valves, turboexpanders, compressors, phase separation vessels, adsorption vessels, interconnecting piping and instrumentation. The closed refrigerant loop may therefore also be in connection with additional equipment comprised within the liquefaction unit. By “closed” herein, is meant that the refrigerant loop containing the first refrigerant is an isolated loop such that the first refrigerant does not undergo intimate mixing with other streams in the apparatus, for example, the hydrogen feed stream, the hydrogen BOG stream, the heated hydrogen BOG stream and the compressed heated hydrogen BOG stream. However, the skilled person will understand that within the closed refrigerant loop, the presence of equipment such as expanders and compressors can cause leakage of small amounts of the first refrigerant from e.g., the joints, valves and seals within the loop. Accordingly, the closed refrigerant loop may contain one or more additional closable inlets (not shown in Figures 2-6) to allow for optional top-up of the first refrigerant, if needed.

The person skilled in the art will readily understand that the liquefaction unit may be varied in many ways.

The liquefaction unit comprises a precooling cold box and a liquefaction cold box, wherein the first refrigerant passes through one or both of the precooling cold box and the liquefaction cold box.

The article "*Hydrogen liquefaction: a review of the fundamental physics, engineering practice and future opportunities*" by S. Al Ghafri et al., Energy Environ. Sci., 2022, 15, 2690-2731 (available through DOI:10.1039/d2ee00099g) defines that the purpose of a cold box is to: "*minimise heat leakage into the cryogenic equipment*", which to a person skilled in the art is understood to be equipment at, or below, a temperature of 120 K. That is to say, the precooling and liquefaction cold boxes in a hydrogen liquefaction unit are not part of its process system, but they are part of its mechanical insulation system. Al Ghafri et al. further describe industrial cold boxes to be: "*cylindrical or rectangular vessels designed to store the main cryogenic equipment such as plate fin heat exchangers; turbine expanders; adsorber and phase separation vessels.*" Such cold box vessels are typically filled with insulation material like perlite, typically comprise multi-layer superinsulation, and are maintained under an inert, or vacuumized atmosphere. When a hydrogen liquefaction unit comprises both an inerted precooling cold box and a vacuumized liquefaction cold box, the precooling cold box comprises the cryogenic equipment at a temperature above the ambient pressure boiling point of the inertization gas used. For example, this temperature is 77 K for nitrogen, and 87 K for argon. The cryogenic equipment at a lower temperature will then reside in the liquefaction cold box.

In the present invention, the hydrogen feed stream provided in step (a) is cooled in the precooling cold box, thereby obtaining a pre-cooled hydrogen stream having an intermediate temperature.

The pre-cooled hydrogen stream having an intermediate temperature is still gaseous. Typically, the pre-cooled hydrogen stream has a temperature in the range of from -203 to -123 °C (70 to 150 K), preferably -198 to -153 °C (75 to 120 K).

The person skilled in the art will readily understand that the precooling cold box can be varied in many ways.

The precooling cold box may comprise one or more heat exchangers. Also, the precooling cold box may comprise components that enable isenthalpic and/or isentropic expansion. Examples of different pre-cooling line-ups have for example been described in "*Hydrogen liquefaction: a review of the fundamental physics, engineering practice and future opportunities*" by S. Al Ghafri et al., Energy Environ. Sci., 2022, 15, 2690-2731 (available through DOI:10.1039/d2ee00099g), in particular in Figures 6 to 10.

In the liquefaction cold box, the pre-cooled hydrogen stream having an intermediate temperature is cooled further, thereby obtaining an at least partly liquefied hydrogen stream (and preferably a fully liquefied hydrogen stream).

Again, the person skilled in the art will readily understand that the liquefaction cold box can be varied in many ways. The liquefaction cold box may comprise one or more heat exchangers. Also, the liquefaction cold box may comprise components which enable isenthalpic and/or isentropic expansion, e.g. valves or expanders. Also, part of the cooling in the liquefaction cold box may (and

typically will) be achieved by expansion of the hydrogen feed stream. Suitable, non-limiting examples of a liquefaction line-up have for example been disclosed in Figs. 6-10 of the above-mentioned article by S. Al Ghafri et al.

According to a preferred embodiment of the process according to the present invention, the liquefaction unit uses a second refrigerant and wherein the second refrigerant passes through one or both of the precooling cold box and the liquefaction cold box.

The person skilled in the art will readily understand that the first refrigerant and second refrigerant may be varied in many ways and are not particularly limited. Also, further refrigerants may be present, in addition to the first and second refrigerants. The composition of the first, second and further refrigerants will depend on *inter alia* where in the liquefaction unit the refrigerants will be used.

According to a preferred embodiment of the process according to the present invention, the first refrigerant is selected from the group consisting of nitrogen, one or more hydrocarbons, argon, hydrogen, helium, neon or a mixture thereof, preferably selected from the group consisting of hydrogen, helium, neon or a mixture thereof.

Further, it is preferred that the second refrigerant is selected from the group consisting of nitrogen, one or more hydrocarbons, argon, hydrogen, helium, neon or a mixture thereof, preferably selected from the group consisting of nitrogen, one or more hydrocarbons, argon or a mixture thereof. Typically, the second refrigerant will comprise nitrogen or nitrogen in mixture with other components. Suitable refrigerant compositions that can be

used as the second refrigerant have for example been disclosed in WO 2017/072221 A1 (also published as EP 3368630 A1).

According to an embodiment of the process according to the present invention, the first refrigerant does not pass through the liquefaction cold box.

According to an embodiment of the process according to the present invention, the second refrigerant does not pass through the liquefaction cold box.

The person skilled in the art will understand that the external heat exchanger (in which the compressed first refrigerant is cooled after leaving the liquefaction unit) is not particularly limited, provided that the external heat exchanger is external to the liquefaction unit (i.e. does not form part of the liquefaction unit).

In step (c) of the process according to the present invention, a hydrogen BOG stream is provided.

Typically, the hydrogen BOG stream provided in step (c) is a hydrogen BOG stream originating from liquid hydrogen handling and storage operation, and hence has a high hydrogen content and is low in impurities (which would otherwise freeze in the conduits to the storage tank). The hydrogen BOG stream may originate from (a combination of) various sources, such as hydrogen BOG generated during cooling down of the hydrogen, heat ingress into several parts of the hydrogen supply chain, depressurization of storage tanks, etc. Preferably, the hydrogen BOG originates from a liquid hydrogen storage tank, preferably from a liquid hydrogen storage tank that is being filled with liquid hydrogen (thereby generating hydrogen BOG).

Preferably, the hydrogen BOG stream provided in step (c) originates from one or more storage tanks, which one or more storage tanks are filled with liquid hydrogen obtained in step (b).

These storage tanks may be 'mobile' tanks for storing liquid hydrogen (which can be transported to a different location) or 'static' or 'non-mobile' tanks for storing liquid hydrogen (which will not be transported to a different location but stay with the hydrogen liquefaction process unit).

Hereinafter the mobile tanks will be referred to with 'first storage tanks', whilst the static tanks will be referred to with 'second storage tanks'.

According to a preferred embodiment of the process according to the present invention, the liquefied hydrogen stream obtained in step (b) is temporarily stored in a (static) second storage tank, and wherein one or more (mobile) first storage tanks are filled with liquid hydrogen from the second storage tank.

Typically, if both first and second storage tanks are present, the volume of the second storage tank is bigger than the volume of the first storage tank(s).

According to a preferred embodiment of the process according to the present invention (and to reflect the typical large BOG volumes as being handled by the process according to the present invention), during filling with liquid hydrogen the amount of hydrogen BOG originating from the one or more storage tanks is at least 1000 kg/day for at least one storage tank, preferably per individual storage tank.

Also, it is preferred that the second storage tank has a volume of at least 1000 m^3, preferably at least

1500 m^3, more preferably at least 2000 m^3, even more preferably at least 2500 m^3.

Preferably, the hydrogen BOG stream provided in step (c) comprises at least 99.0 wt.% hydrogen, preferably at least 99.8 wt.%, more preferably at least 99.9 wt.%. Furthermore, it is preferred that the hydrogen BOG gas stream provided in step (c) comprises at least 90 wt.% para-hydrogen, preferably at least 95 wt.%.

Although the temperature of the hydrogen BOG stream provided in step (c) is not particularly limited and may be from low temperatures of ~ -259 °C (~14 K) up to ambient (~25 °C (298 K)) temperature, preferably the hydrogen BOG stream provided in step (c) has a temperature in the range of -259 to -213 °C (14 to 60 K), preferably below -233 °C (below 40 K). This reflects a typical temperature of a hydrogen BOG stream coming from a liquid hydrogen storage tank, in particular when generated during the filling/loading of said liquid hydrogen storage tank.

Also, although the pressure of the hydrogen BOG stream provided in step (c) is not particularly limited, preferably the hydrogen BOG stream provided in step (c) has a pressure in the range of 1.0-6.0 bara, preferably at most 3.0 bara.

The hydrogen BOG stream provided in step (c) is fed to the external heat exchanger. Preferably, the hydrogen BOG stream is fed directly to the external heat exchanger. By “directly” is meant that the hydrogen BOG stream provided in step (c) does not pass through any liquefaction unit heat exchangers, precooling cold box or liquefaction cold box prior to the external heat exchanger.

In step (d) of the process according to the present invention, the hydrogen BOG stream provided in step (c) is heated in the external heat exchanger against the compressed first refrigerant, thereby obtaining a heated hydrogen BOG stream. If desired, the hydrogen BOG stream may be heated against other streams as well, in addition to heat exchanging against the compressed first refrigerant. Such additional heating may take place in the external heat exchanger or in one or more separate heat exchangers. However, according to an especially preferred embodiment according to the present invention, the hydrogen BOG stream is not heated in the precooling cold box or the liquefaction cold box.

Generally, the heated hydrogen BOG stream has a temperature of -150 to 55 °C (123 to 328 K), preferably -40 to 55 °C (233 to 328 K), more preferably -20 to 40 °C (253 to 313 K).

Further, the heated hydrogen BOG stream typically has a pressure of 1.0 to 6.0 bara.

In step (e) of the process according to the present invention, the heated hydrogen BOG stream is compressed, thereby obtaining a compressed heated hydrogen BOG stream. Generally, compressed heated hydrogen BOG stream has a pressure in the range of 15-80 bara, preferably below 50 bara, more preferably below 35 bara.

In step (f) of the process according to the present invention, the compressed heated hydrogen BOG stream obtained in step (e) is combined with the hydrogen feed stream provided in step (a). Preferably, the compressed heated hydrogen BOG stream and the hydrogen feed stream are combined upstream of the (precooling cold box of the) liquefaction unit and enter the liquefaction unit as a combined stream.

As described hereinbefore, in another aspect, the present invention provides an apparatus suitable for performing the process for handling a hydrogen BOG (boil-off gas) stream according to the present invention, the apparatus at least comprising:

- a liquefaction unit comprising a precooling cold box and a liquefaction cold box, for cooling a hydrogen feed stream to be liquefied, using at least a first refrigerant, to obtain an at least partly liquefied hydrogen stream;
- a compressor for compressing the first refrigerant after the first refrigerant has left the liquefaction unit;
- an external heat exchanger for cooling the first refrigerant after the first refrigerant has left the compressor;
- one or more storage tanks that can be filled with liquefied hydrogen and can provide a hydrogen BOG stream;

wherein in the external heat exchanger the hydrogen BOG stream can be heated against the first refrigerant, thereby obtaining a heated hydrogen BOG stream;

- a compressor for compressing the heated hydrogen BOG stream, thereby obtaining a compressed heated hydrogen BOG stream; and
- a joint for combining the compressed heated hydrogen BOG stream with the hydrogen feed stream, wherein the first refrigerant is in a closed refrigerant loop comprising the external heat exchanger, the compressor and the liquefaction unit.

Preferably, the apparatus further comprises a second storage tank for temporarily storing the liquefied hydrogen obtained in the liquefaction unit, wherein one

or more first storage tanks can be filled with liquid hydrogen from the second storage tank.

Hereinafter, the present invention will be further illustrated by the following non-limiting drawings: Figures 2 to 6.

For the purpose of this description, same reference numbers refer to same or similar components.

The flow scheme of Figure 2 generally referred to with reference number 1, shows a liquefaction unit 2, an external heat exchanger 3, compressors 4 and 5, several (mobile) first storage tanks 6 for storing liquefied hydrogen, and a joint 9.

During use of the line-up of Fig. 2, a hydrogen feed stream 10 to be liquefied is provided. The hydrogen feed stream 10 is fed (as stream 15) to the liquefaction unit 2. In the liquefaction unit 2, the hydrogen feed stream is cooled using at least a first refrigerant 30, thereby obtaining an at least partly liquefied stream 20.

The liquefaction unit 2 uses at least the first refrigerant 30, which is cycled in a first refrigerant cycle. Compressor 4 forms part of the first refrigerant cycle. The first refrigerant cycle will typically contain other components that enable isenthalpic and/or isentropic expansion as well.

The first refrigerant is, after leaving the liquefaction unit 2 (as stream 40), compressed in compressor 4 to obtain a compressed first refrigerant 50. The compressed first refrigerant 50 is cooled in the external heat exchanger 3 (which does not form part of the liquefaction unit 2) before being returned (as stream 30) to the liquefaction unit 2.

In the embodiment of Fig. 2, the liquefied hydrogen stream 20 is used to directly fill the mobile first

storage tanks 6. During the filling of the mobile first storage tanks 6, a relatively large amount of hydrogen BOG (stream 60 in Fig. 2) is generated.

After completion of the filling of the first hydrogen storage tanks 6, these tanks (which may for example be placed on a vessel or the like) may be transported to their intended destination.

The hydrogen BOG stream 60 is heated in the external heat exchanger 3 against the compressed first refrigerant 50, thereby obtaining a heated hydrogen BOG stream 70. The heated hydrogen BOG stream 70 is compressed in compressor 5, thereby obtaining a compressed heated hydrogen BOG stream 80. Then, the compressed heated hydrogen BOG stream 80 is combined with the hydrogen feed stream 10 at joint 9 and then passed to the liquefaction unit 2 as combined stream 15.

Fig. 3 schematically shows a (more detailed) flow scheme of a second embodiment of the process according to the present invention.

In the embodiment of Fig. 3, the liquefaction unit 2 comprises a precooling cold box 21 and a liquefaction cold box 22. The liquefaction unit 2 uses both the first refrigerant 30 and a second refrigerant 200.

The first refrigerant 30 passes through both of the precooling cold box 21 and the liquefaction cold box 22, whilst the second refrigerant 200 passes through the precooling cold box 21 but not through the liquefaction cold box 22.

In the embodiment of Fig. 3, the first refrigerant 30 is preferably selected from the group consisting of hydrogen, helium, neon or a mixture thereof, whilst the second refrigerant 200 is preferably selected from the

group consisting of nitrogen, one or more hydrocarbons, argon or a mixture thereof.

During use of the line-up of Fig. 3, the hydrogen feed stream 10 (fed as stream 15 to the liquefaction unit 2) is cooled in the precooling cold box 21 thereby obtaining a pre-cooled hydrogen stream 15' having an intermediate temperature.

The precooling cold box 21 uses the first refrigerant 30, which is cycled in a first refrigerant cycle, and the second refrigerant 200, which is cycled in a second refrigerant cycle. Compressor 4 forms part of the first refrigerant cycle. Compressor 7 forms part of the second refrigerant cycle. The first and second refrigerant cycles will typically contain other components that enable isenthalpic and/or isentropic expansion as well.

After exiting the precooling cold box 21, the pre-cooled hydrogen stream 15' is further cooled in the liquefaction cold box 22 thereby obtaining the at least partially liquefied hydrogen stream 20.

Fig. 4 schematically shows a (more detailed) flow scheme of a third embodiment of the process according to the present invention.

In the embodiment of Fig. 4, the liquefaction unit 2 again – like Fig. 3 - comprises a precooling cold box 21 and a liquefaction cold box 22, and a first refrigerant 30 and a second refrigerant 200.

However, in Fig. 4 it is the second refrigerant 200 that passes through both the precooling cold box 21 and the liquefaction cold box 22, whilst the first refrigerant 30 passes through the precooling cold box 21, but not through the liquefaction cold box 22.

In the embodiment of Fig. 4, the second refrigerant 200 is preferably selected from the group consisting of

hydrogen, helium, neon or a mixture thereof, whilst the first refrigerant 30 is preferably selected from the group consisting of nitrogen, one or more hydrocarbons, argon or a mixture thereof.

Fig. 5 schematically shows a flow scheme of a fourth embodiment of the process according to the present invention.

In the embodiment of Fig. 5, the liquefied hydrogen stream 20 is temporarily stored in (static or non-mobile) second storage tanks 8. These second storage tanks 8 will not be transported to a different location but stay with the hydrogen liquefaction process unit 1. The second storage tanks 8 are bigger (as in: have a larger internal volume) than the first storage tanks 6. The one or more first storage tanks 6 are filled with liquid hydrogen from the second storage tanks 8. The person skilled in the art will understand that the filling of the second storage tanks 8 may also result in the generation of hydrogen BOG; these hydrogen BOG streams (not shown in Fig. 5) may be handled as well by passing to line 60.

The person skilled in the art will understand that the concept of using (static or non-mobile) second storage tanks 8 as shown in Fig. 5 is applicable to the embodiments as shown in Figs. 3 and 4 as well.

Fig. 6 schematically shows a flow scheme of a fifth embodiment of the process according to the present invention. In the embodiment of Fig. 6, the liquefied hydrogen stream 20 is used to fill the static second storage tank 8. Again, during the filling of the static second storage tank 8, a hydrogen BOG stream 60 is generated which is passed via the external heat exchanger 3 and the compressor 5 for combination with the hydrogen feed stream 10 at joint 9. The mobile first storage tank

6 is filled with liquid hydrogen from the static second storage tank 8. Any hydrogen BOG generated during the filling of first storage tank 6 is sent back to the second storage tank 8 and passed on with the hydrogen BOG stream 60 generated in the second storage tank 8. If desired, part of the hydrogen BOG stream from the first storage tank 6 may be recondensed in the second storage tank 8.

Again, the person skilled in the art will understand that the concept of using (static or non-mobile) second storage tanks 8 as shown in Fig. 6 is applicable to the embodiments as shown in Figs. 3 and 4 as well.

Discussion

As can be seen from Figs. 2-6, the process according to the present invention allows for a surprisingly simple and effective way of handling a hydrogen BOG stream.

An important advantage of the present invention is that intermittent or variable amounts and/or temperatures of hydrogen BOG can be handled, without severe implications on e.g. the heat exchanger equipment in the precooling and/or the liquefaction cold box (which would occur in case hydrogen BOG would directly be sent to the precooling and/or the liquefaction cold box).

Further, the process according to the present invention works irrespective of the pressure of BOG stream 60 (no specific pressure limits to be met).

Also, there is no need to build/operate large (subcooled) LH_2 tanks for BOG recondensation.

Furthermore, the present invention reduces or even negates the need to vent large amounts of BOG, which venting would be environmentally and economically undesirable.

The person skilled in the art will readily understand that many modifications may be made without departing from the scope of the invention. Further, the person skilled in the art will readily understand that, while the present invention in some instances may have been illustrated making reference to a specific combination of features and measures, many of those features and measures are functionally independent from other features and measures given in the respective embodiment(s) such that they can be equally or similarly applied independently in other embodiments.

C L A I M S

1. A process for handling a hydrogen BOG (boil-off gas) stream, the process at least comprising the steps of:

(a) providing a hydrogen feed stream (10) to be liquefied;

(b) cooling the hydrogen feed stream (10) provided in step (a) in a liquefaction unit (2) comprising a precooling cold box (21) and a liquefaction cold box (22), using at least a first refrigerant (30) thereby obtaining an at least partly liquefied hydrogen stream (20), wherein the first refrigerant (40) is, after leaving the liquefaction unit (2), compressed in a compressor (4) to obtain a compressed first refrigerant (50) and cooled in an external heat exchanger (3) before being returned to the liquefaction unit (2);

(c) providing a hydrogen BOG stream (60);

(d) heating the hydrogen BOG stream (60) provided in step (c) in the external heat exchanger (3) against the compressed first refrigerant (50), thereby obtaining a heated hydrogen BOG stream (70);

(e) compressing the heated hydrogen BOG stream (70), thereby obtaining a compressed heated hydrogen BOG stream (80); and

(f) combining the compressed heated hydrogen BOG stream (80) obtained in step (e) with the hydrogen feed stream (10) provided in step (a); and

wherein the first refrigerant (30,40,50) is in a closed refrigerant loop comprising the external heat exchanger (3), the compressor (4) and the liquefaction unit (2).

2. The process according to claim 1, wherein the first refrigerant (30) passes through one or both of the

precooling cold box (21) and the liquefaction cold box (22).

3. The process according to claim 1 or 2, wherein the liquefaction unit (2) uses a second refrigerant (200) and wherein the second refrigerant (200) passes through one or both of the precooling cold box (21) and the liquefaction cold box (22).

4. The process according to any one of the preceding claims, wherein the first refrigerant (30) is selected from the group consisting of nitrogen, one or more hydrocarbons, argon, hydrogen, helium, neon or a mixture thereof, preferably selected from the group consisting of hydrogen, helium, neon or a mixture thereof.

5. The process according to claim 3 or 4, wherein the second refrigerant (200) is selected from the group consisting of nitrogen, one or more hydrocarbons, argon, hydrogen, helium, neon or a mixture thereof, preferably selected from the group consisting of nitrogen, one or more hydrocarbons, argon or a mixture thereof.

6. The process according to any one of claim 2-5, wherein the first refrigerant (30) does not pass through the liquefaction cold box (22).

7. The process according to any one of claim 2-5, wherein the second refrigerant (200) does not pass through the liquefaction cold box (22).

8. The process according to any one of the preceding claims, wherein the hydrogen BOG stream (60) provided in step (c) originates from one or more storage tanks (6,8), which one or more storage tanks (6,8) are filled with liquid hydrogen (20) obtained in step (b).

9. The process according to claim 8, wherein the liquefied hydrogen stream obtained in step (b) is temporarily stored in a second storage tank (8), and

wherein one or more first storage tanks (6) are filled with liquid hydrogen from the second storage tank (8).

10. The process according to claim 8 or 9, wherein during filling with liquid hydrogen the amount of hydrogen BOG originating from the one or more storage tanks (6,8) is at least 1000 kg/day for at least one storage tank (6,8).

11. The process according to any one of claims 9 or 10, wherein the second storage tank (8) has a volume of at least 1000 m^3, preferably at least 1500 m^3, more preferably at least 2000 m^3, even more preferably at least 2500 m^3.

12. The process according to any one of the preceding claims, wherein the hydrogen BOG stream (60) provided in step (c) comprises at least 99.0 wt.% hydrogen, preferably at least 99.8 wt.%, more preferably at least 99.9 wt.%.

13. The process according to any one of the preceding claims, wherein the hydrogen BOG stream (60) provided in step (c) has a temperature in the range of -259 to -213 °C (14 to 60 K), preferably below -233 °C (40 K).

14. The process according to any one of the preceding claims, wherein the hydrogen BOG stream (60) provided in step (c) has a pressure in the range of 1.0-6.0 bara, preferably at most 3.0 bara.

15. An apparatus (1) suitable for performing the process for handling a hydrogen BOG (boil-off gas) stream according to any one of the preceding claims 1-14, the apparatus (1) at least comprising:

- a liquefaction unit (2) comprising a precooling cold box (21) and a liquefaction cold box (22), for cooling a hydrogen feed stream (10) to be liquefied, using at least a first refrigerant (30), to obtain an at least partly liquefied hydrogen stream (20);

- a compressor (4) for compressing the first refrigerant (40) after the first refrigerant has left the liquefaction unit (2);

- an external heat exchanger (3) for cooling the first refrigerant (50) after the first refrigerant has left the compressor (4);

- one or more storage tanks (6,8) that can be filled with liquefied hydrogen and can provide a hydrogen BOG stream (60);

wherein in the external heat exchanger (3) the hydrogen BOG stream (60) can be heated against the first refrigerant (50), thereby obtaining a heated hydrogen BOG stream (70);

- a compressor (5) for compressing the heated hydrogen BOG stream (70), thereby obtaining a compressed heated hydrogen BOG stream (80); and

- a joint (9) for combining the compressed heated hydrogen BOG stream (80) with the hydrogen feed stream (10),

wherein the first refrigerant (30,40,50) is in a closed refrigerant loop comprising the external heat exchanger (3), the compressor (4) and the liquefaction unit (2).

16. The apparatus according to claim 15, further comprising a second storage tank (8) for temporarily storing the liquefied hydrogen (20) obtained in the liquefaction unit (2), wherein one or more first storage tanks (6) can be filled with liquid hydrogen from the second storage tank (8).