

- 1 -

A PROCESS FOR STORING LIQUID HYDROGEN

Field of the Invention

The present invention relates to a process for storing liquid hydrogen in a storage tank.

Background of the Invention

5 Hydrogen is seen as one of the most promising energy carriers for a decarbonized energy system. Efficient transport and storage of liquid hydrogen (LH₂) are seen as critical to its large-scale adoption.

10 One of the main challenges of the storage of LH₂ is the handling of hydrogen boil-off gas (BOG) losses due to the requirement to cool down, heat ingress, the need to depressurize storage tanks, etc.

15 US 6151900 A describes a method for cooling a first cryogenic fluid in a vessel, which method comprises the steps of: a. directing a second cryogenic fluid into the first cryogenic fluid, wherein the second cryogenic fluid has a boiling point that is lower than the boiling point of the first cryogenic fluid, whereby the first cryogenic fluid is cooled and a portion of the second cryogenic
20 fluid becomes a gas; and b. releasing the gas from the vessel. In an aspect of US 6151900 A, the second cryogenic fluid may be directed into the vessel through a diffuser located in the bottom of the vessel. In a further aspect of US 6151900 A, the first cryogenic
25 liquid may be hydrogen and the second cryogenic liquid may be helium.

30 US 6151900 A further describes a cryogenic fluid cooling system comprising a cryogenic fluid holding vessel, first and second cryogenic fluid supplies, a cryogenic fluid feed line, and a fluid flow control

- 2 -

system. The cryogenic fluid holding vessel comprises a cryogenic fluid inlet and a gas release outlet. The cryogenic fluid feed line comprises an outlet connected to the cryogenic fluid holding vessel inlet and an inlet
5 connected to the first and second cryogenic fluid supplies. The fluid flow control system is functionally connected to the first and second cryogenic fluid supplies.

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 LH₂ system using IRAS (Integrated Refrigeration and Storage) technology aiming at ZBO (zero boil-off) operations, i.e. eliminating the occurrence of hydrogen BOG.
10

A problem with 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 transport and holding operations, it does not completely eliminate boil-off generation, in particular in hydrogen transfer operations (i.e. moving the LH₂ from one storage tank to another). Hence,
15 20 hydrogen boil-off handling will still be required.

A further problem with the above IRAS technology is the potential to create a vacuum if too much BOG is reliquefied, which would require internally reinforced tanks.
25

It is desirable to solve, minimize or at least reduce one or more of the above problems associated with the storage of LH₂.

It is also desirable to provide alternative processes for storing LH₂.
30

Summary of the Invention

- 3 -

One or more of the above or other objects may be achieved according to the present invention by providing a process for storing LH₂ in a storage tank, the process at least comprising the steps of:

- 5 (a) providing a first storage tank containing LH₂;
- (b) feeding liquid helium (LHe) into the first storage tank at an inlet below a liquid level of the LH₂ in the first storage tank and allowing the LHe to vaporize and bubble through the LH₂ in the first storage
- 10 tank; and
- (c) feeding LHe into the first storage tank at an inlet at or near the top of the first storage tank.

The present invention further provides an apparatus suitable for storing LH₂ in a storage tank, the apparatus at least comprising:

15

- a first storage tank containing LH₂;
- a second storage tank containing LHe;

wherein the first storage tank has a first inlet for receiving LHe from the second storage tank below the liquid level of LH₂ in the first storage tank; and

20 wherein the first storage tank has a second inlet at or near the top for receiving LHe from the second storage tank in a vapour space above the liquid level of LH₂ in the first storage tank.

25 Brief Description of the Figures

Fig. 1 schematically a flow scheme of the process for storing LH₂ according to the present invention,

Fig. 2 schematically a flow scheme of the process for cooling down a storage tank for LH₂ according to the present invention.

30

While the present disclosure is susceptible to various modifications and alternative forms, specific

- 4 -

example embodiments have been shown in the figures and are herein described in more detail.

It should be understood, however, that the description of specific example 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 using the cooling capacity of the LHe, the occurrence of hydrogen BOG can be avoided or at least minimized in a surprisingly simple manner. As a result, no venting of hydrogen BOG or reprocessing thereof outside the tank using (very large) compression systems are needed.

A further advantage of the process according to the present invention is that the risk of a sub-atmospheric pressure (i.e. below 1.0 bara) can be avoided, thereby not requiring special internal reinforcement of the first storage tank.

Another advantage of the process according to the present invention is that a cold, cryogenic blanket of helium vapour may be formed in a vapour space above the liquid level of the LH₂ in the first storage tank. The cold, cryogenic blanket of helium vapour preferably has a temperature of 10-15K. The combination of temperature and pressure of the helium vapour in the cryogenic blanket is chosen such that it keeps the below-situated LH₂ in liquid state.

An important advantage of the formation of the cryogenic blanket of helium vapour in the vapour space is that it allows for a safe operation in case of pressure

- 5 -

increase in the storage tank. This, as when the pressure in said vapour space would increase such that a pressure relief valve would be activated, first relatively harmless helium vapour would leave the storage tank
5 thereby giving adequate time to the operator to manage the pressure increase before any hydrogen would leave the storage tank via the pressure relief valve. Also, the cryogenic blanket of helium vapour (preferably having a temperature of 10-15K) allows to handle relatively warm
10 LH₂ of up to 26K by keeping the LH₂ cold or further cooled and bringing down the temperature thereof.

In step (a) of the process according to the present invention, a first storage tank containing LH₂ is provided.

15 The person skilled in the art will readily understand that the first (hydrogen) storage tank can vary widely.

Also, the composition of the LH₂ in the first storage tank can vary widely. The composition may consist of ortho- or para-hydrogen or contain mixtures thereof.
20 Preferably, the LH₂ in the first storage tank comprises at least 95.0 wt.% para-hydrogen, more preferably at least 99.9 wt.% para-hydrogen.

Also, it is preferred that the LH₂ in the storage tank has a temperature of from 17 to 26K, preferably
25 below 23K.

In step (b) of the process according to the present invention, LHe is fed into the first storage tank at an inlet below a liquid level of the LH₂ in the first storage tank and the LHe is allowed to vaporize and
30 bubble through the LH₂ in the first storage tank. By the vaporization of the LHe, the LH₂ is cooled.

- 6 -

Typically, in step (b) the LHe is fed into the first storage tank near the bottom of the first storage tank.

Although the LHe being fed into the first storage tank is not particularly limited, the LHe being fed in
5 step (b) comprises at least 99 wt.% helium. Further, it is preferred that the LHe being fed in step (b) is colder than the LH₂ in the first storage tank. Preferably, the temperature of the LHe is between 0 to 4.2K, preferably above 1.8K.

10 According to an especially preferred embodiment according to the present invention, the LHe being fed in step (b) originates from a second (helium) storage tank containing LHe.

Preferably, the LHe being fed in step (b) is fed as
15 droplets having a maximum diameter of 1 mm. Typically, the droplets have a VMD (Volume Median Diameter) of 0.404 mm to 0.665 mm as determined according to the ASABE S572.1 standard (i.e. a 'Very Coarse' or 'Extremely Coarse' spray). This will assist in the vaporization
20 (atomization) of the LHe in the LH₂.

As mentioned above, in order to perform cryogenic bubbling, the LHe is fed in step (b) at an inlet below a liquid level of the LH₂ in the first storage tank. Preferably, for particularly advantageous cryogenic
25 bubbling, the LHe is fed in step (b) at a height between a third of the height, as seen from the bottom of the LH₂, of the liquid level of the LH₂ and the liquid level of the LH₂. Hereby, any temperature stress on the inner vessel of the tank caused by contact with sinking
30 (heavier) LHe after being fed into the first storage tank is minimized.

According to a preferred embodiment of the process according to the present invention, the first storage

- 7 -

tank is operated at a pressure in the range of 30 to 500 kPag, preferably at most 100 kPag), preferably forming a cryogenic blanket of helium vapour in the vapour space above the liquid level of the LH₂ in the first storage tank, wherein the cryogenic blanket of helium vapour preferably has a temperature of 10-15K. The combination of temperature and pressure of the (colder) helium vapour in the cryogenic blanket is chosen such that it keeps the below-situated LH₂ in liquid state. Preferably, the operation pressure of the first storage tank is kept at at least 15 kPag above the saturation pressure of the LH₂ stored.

An important advantage of the formation of the cryogenic blanket of helium vapour in the vapour space is allows for a safe operation in case of pressure increase in the storage tank. This, as when the pressure in said vapour space would increase such that a relief valve would be activated, first relatively harmless helium vapour would leave the storage tank thereby giving adequate time to the operator to manage the pressure increase before any hydrogen would leave the storage tank via the relief valve and hence through a vent mast. Vent mast releases of cryogenic hydrogen would have various risks that are yet to be understood by the hydrogen handling industry.

Although the feeding of LHe into the first storage tank in step (c) is not particularly limited to a specific manner of feeding, it typically occurs by means of spraying in a vapour space above the liquid level of LH₂ in the first storage tank. Preferably the LHe fed in step (c) originates from the second (helium) storage tank as well.

- 8 -

The feeding of LHe in step (c) assists in forming a 'blanket' of cold helium vapour (preferably 10-15K at a pressure of from 4 to 100 kPag, preferably above 20 and below 40 kPag) above the liquid level of the LH₂, thereby preventing or at least minimizing that hydrogen molecules pass from the liquid level into the vapour space above the liquid level. For the sake of stabilization of the cold helium vapour blanket, the operating pressure can go up to or close to the pressure that activates the pressure relief valve (usually 400 kPag). Preferably, the operation pressure of the first storage tank is kept at at least 15 kPag above the saturation pressure of the LH₂ stored.

Further it is preferred that gaseous helium is removed at an outlet at or near the top of the first storage tank, recondensed and sent to the second storage tank. The gaseous helium is removed from a vapour space above the liquid level of the LH₂ in the first storage tank. Usually, the removed gaseous helium contains less than 1 vol.% hydrogen, preferably no hydrogen at all. This, as the removed gaseous helium (which is removed from the helium vapour blanket) is in a 'cryogenic' state (preferably at a temperature of 10-15K), i.e. it keeps the below-situated LH₂ in liquid state.

As mentioned hereinbefore, in another aspect, the present invention provides an apparatus suitable for storing LH₂ in a storage tank.

The apparatus according to the present invention can comprise more than one first (hydrogen) storage tanks and/or more than one second (helium) storage tanks.

Typically, the first inlet of the first storage tank is placed at or near the bottom of the first storage

- 9 -

tank. Also, the LHe fed via the first inlet is usually sprayed.

5 The first storage tank has a second inlet at or near the top for receiving LHe from the second storage tank in a vapour space above the liquid level of LH₂ in the first storage tank.

Further it is preferred that the first storage tank has an outlet for gaseous helium, which outlet is fluidly connected to an inlet of the second storage tank.

10 Typically, the outlet for gaseous helium is placed at or near the top of the first storage tank. Usually, the gaseous helium is, after being removed from the first storage tank and before being fed into the second storage tank, recondensed. As recondensing of helium is known in
15 the art, this is not further discussed here. As a mere example, a commercially available helium recovery system such as a Helial/Hylial liquefier (Air Liquide Advanced Technologies (ALAT), France) can be used for recondensing the helium.

20 In a further aspect, the present invention provides a process for cooling down a storage tank for LH₂, the process comprising at least the steps of:

- (i) providing a (usually empty) first storage tank;
- (ii) feeding the first storage tank with LH₂ via an
25 inlet, whilst allowing hydrogen boil-off gas (BOG) generated during the feeding to leave the first storage tank via an outlet;
- (iii) closing the outlet for hydrogen BOG;
- (iv) feeding LHe into the first storage tank, in a
30 vapour space above the liquid level of the LH₂ in the first storage tank, thereby recondensing hydrogen BOG;
- (v) once the vapour space has a vapour pressure of below 30 kPag, feeding LHe below a liquid level of the

- 10 -

first storage tank and allowing the LHe to vaporize and bubble through the LH₂ in the first storage tank, preferably forming a cryogenic blanket of helium vapour in the vapour space above the liquid level of the LH₂ in the first storage tank. The combination of temperature and pressure of the (colder) helium vapour in the cryogenic blanket is chosen such that it keeps the below-situated LH₂ in liquid state. Preferably, the operation pressure of the first storage tank is kept at at least 15 kPag above the saturation pressure of the LH₂ stored.

Although the type of feeding of LHe in steps (ii) and iv) is not particularly limited to a specific manner of feeding, it preferably occurs by means of spraying.

Typically, in step (iii), the outlet for hydrogen BOG is closed once the vapour space in the first storage tank has reached a pressure of saturation pressure at the loaded LH₂ temperature (preferably between 17K to 26K), preferably 4 kPag to 8 kPag. For a loaded LH₂ temperature of less than 20K, the saturation temperature will be limited to 4 kPag (to prevent that the pressure in the vapour space goes to below atmospheric pressure).

Preferably, in step (iv), already some helium vapour will enter the vapour space above the liquid level in the first storage tank, thereby replacing hydrogen vapour.

Hereinafter, the present invention will be further illustrated with reference to the non-limiting Figures 1 and 2.

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

The flow scheme of Figure 1 generally referred to with reference number 1, shows a first storage tank 2 containing LH₂, a second storage tank 3 containing LHe, a

- 11 -

variable pressure regulator 4, and a helium re-condenser or recovery system 5. The person skilled in the art will understand that more than one first (hydrogen) storage tanks 2 and/or second (helium) storage tanks 3 may be present.

As shown in Fig. 1, the first storage tank 2 contains LH₂ 2a. Above the liquid level 2c of the LH₂ 2a, a vapour space 2b exists. The first storage tank 2 has a first inlet 2d for receiving (usually by means of a spray) LHe via line 30 from the second storage tank 3 below the liquid level 2c of LH₂ 2a in the first storage tank 2. Also, the first storage tank 2 has a second inlet 2e at or near the top of the first storage tank 2 for feeding LHe via line 40 from the second storage tank 3 in the vapour space 2b above the liquid level 2c of LH₂ 2a in the first storage tank 2. Further, the first storage tank 2 has an outlet 2f at or near the top of the storage tank 2 for removing gaseous helium via line 50 from the vapour space 2b.

During use of the embodiment of Fig. 1, LHe is fed via line 30 into the first storage tank 2 already containing LH₂ 2a. The LHe 30 originates from second storage tank 3. The LHe 30 is fed into the first storage tank 2 at inlet 2d below the liquid level 2c of the LH₂ 2a, preferably by means of a spray (not shown). The LHe is allowed to vaporize and bubble through the LH₂ 2a in the first storage tank 2 thereby cooling the LH₂ 2a. The vaporized helium will at some point end up in the vapour space 2b above the liquid level 2c.

As also shown in the embodiment of Fig. 1, LHe is also fed via line 40 into the storage tank 2, via inlet 2e near the top of the first storage tank 2. The LHe 40

- 12 -

originates from the second storage tank 3. The LHe 40 is fed into the first storage tank 2 into the vapour space 2b above the liquid level 2c of the LH₂ 2a, again preferably by means of a spray (not shown).

5 The feeding of LHe 40 into the vapour space 2b above the liquid level 2c assists in forming a cryogenic 'blanket' of cold helium vapour (preferably 10-15K at 30 kPag and an operational pressure of up to 100 kPag) above the liquid level 2c of the LH₂, thereby preventing or at
10 least minimizing that hydrogen molecules pass from the liquid level 2c into the vapour space 2b above the liquid level 2c.

 Gaseous helium is removed via line 50 at an outlet 2f near the top of the first storage tank 2, recondensed in
15 condenser 5 and sent to the second storage tank 3 for reuse. The flow of helium is set by the variable pressure regulator 4 which will be set based on the blanketing process parameters for the temperature of the loaded LH₂ in the tank 2. Typically, and caused by the above
20 'blanket', the removed gaseous helium 50 contains less than 1 vol.% hydrogen or is even substantially free of hydrogen.

 Hence, in one embodiment, the present invention provides a process for storing liquid hydrogen (LH₂) in a
25 storage tank, wherein said process at least comprises the steps of:

- (a) providing a first storage tank 2 containing LH₂ 2a with cryogenic blanketing of vapor space 2b;
- (b) feeding liquid helium (LHe) 30 into the first
30 storage tank 2 at an inlet 2d below a liquid level 2c of the LH₂ 2a in the first storage tank 2 and allowing the

- 13 -

LHe to vaporize and perform cryogenic bubbling through the LH₂ 2a in the first storage tank (2); and

(c) feeding LHe 40 into the first storage tank 2 at an inlet 2e at or near the top of the first storage tank (2.

Fig. 2 shows schematically a flow scheme of the process for cooling down a storage tank for LH₂ according to the present invention.

During use of the embodiment of Fig. 2, LH₂ is fed via line 10 into the (at the start empty) first storage tank 2. The LH₂ 10 is fed via inlet 2g, whilst allowing hydrogen BOG generated during the feeding to leave the first storage tank 2 as stream 20 via an outlet 2h. The hydrogen BOG 20 may be recondensed as desired.

Once an appropriate amount of LH₂ has been fed into the first storage tank 2, the outlet 2h for hydrogen BOG 20 is closed. Preferably, at that time, the vapour space 2b in the first storage tank 2 has a pressure between 4 kPag to 8 kPag.

Then, LHe is fed via line 40 into the first storage tank 2, in the vapour space 2b above the liquid level 2c. Hereby, hydrogen BOG present in the vapour space 2b is recondensed.

Once the vapour space 2b has obtained a vapour pressure of below 30 kPag, LHe 30 is fed into the first storage tank 2, below the liquid level 2c thereof. The LHe is then allowed to vaporize and bubble through the LH₂ 2a in the first storage tank 2 thereby cooling the LH₂ and balancing the heat ingress into the tank.

Preferably, a cryogenic blanket of helium vapour is formed in the vapour space 2b above the liquid level 2c of the LH₂ 2a in the first storage tank 2, thereby

- 14 -

preventing or at least minimizing that hydrogen molecules pass from the liquid level 2c into the vapour space 2b above the liquid level 2c.

5 This process will effectively minimize or even nullify the heat ingress into the tank 2 and utilize the heat extraction at low temperatures using commercially available, off-the-shelf helium recovery systems.

Discussion

10 As can be seen from Fig. 1, the present invention provides a surprisingly simple and effective way of storing LH₂. An important advantage of the present invention is that no venting of hydrogen BOG or reprocessing thereof outside the tank using (very large) compression systems are needed.

15 Furthermore, as can be seen from Fig. 2, the present invention provides a surprisingly simple and effective way of cooling down a storage tank for LH₂ and minimising hydrogen BOG.

20 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
25 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.

30

- 15 -

C L A I M S

1. A process for storing liquid hydrogen (LH₂) in a storage tank (2), the process at least comprising the steps of:

(a) providing a first storage tank (2) containing LH₂
5 (2a);

(b) feeding liquid helium (LHe; 30) into the first storage tank (2) at an inlet (2d) below a liquid level (2c) of the LH₂ (2a) in the first storage tank (2) and allowing the LHe to vaporize and bubble through the LH₂
10 (2a) in the first storage tank (2); and

(c) feeding LHe (40) into the first storage tank (2) at an inlet (2e) at or near the top of the first storage tank (2).

2. The process according to claim 1, wherein the LH₂
15 (2a) in the storage tank (2) has a temperature of from 17 to 26K, preferably below 23K.

3. The process according to claim 1 or 2, wherein the LHe (30) being fed in step (b) comprises at least 99 wt.% helium.

20 4. The process according to any one of the preceding claims, wherein the LHe (30) being fed in step (b) is colder than the LH₂ (2a) in the first storage tank (2).

5. The process according to any one of the preceding claims, wherein the LHe (30) being fed in step (b)
25 originates from a second storage tank (3) containing LHe.

6. The process according to any one of the preceding claims, wherein the LHe (30) being fed in step (b) is fed as droplets having a maximum diameter of 1 mm.

7. The process according to any one of the preceding
30 claims, wherein the LHe (30) is fed in step (b) at a

- 16 -

height between a third of the height, as seen from the bottom of the LH₂ (2a), of the liquid level (2c) of the LH₂ (2a) and the liquid level (2c) of the LH₂ (2a).

5 8. The process according to any one of the preceding claims, wherein the first storage tank (2) is operated at a pressure in the range of 30 to 500 kPag, preferably at most 100 kPag), preferably forming a cryogenic blanket of helium vapour in the vapour space (2b) above the liquid level (2c) of the LH₂ (2a) in the first storage tank (2).

10 9. The process according to any of the preceding claims, wherein gaseous helium (50) is removed at an outlet (2f) at or near the top of the first storage tank (2), recondensed and sent to the second storage tank (3).

15 10. An apparatus (1) suitable for storing LH₂ in a storage tank, the apparatus at least comprising:

- a first storage tank (2) containing LH₂ (2a);
- a second storage tank (3) containing LHe;

20 wherein the first storage tank (2) has a first inlet (2d) for receiving LHe (30) from the second storage tank (3) below the liquid level (2c) of LH₂ (2a) in the first storage tank (2); and

25 wherein the first storage tank (2) has a second inlet (2e) at or near the top for receiving LHe (40) from the second storage tank (3) in a vapour space (2b) above the liquid level (2c) of LH₂ (2a) in the first storage tank (2).

30 11. The apparatus (1) according to claim 10, wherein the first storage tank (2) has an outlet (2f) for gaseous helium, which outlet (2f) is fluidly connected to an inlet of the second storage tank (3).

12. A process for cooling down a storage tank for LH₂, the process comprising at least the steps of:

- 17 -

- (i) providing a first storage tank (2);
- (ii) feeding the first storage tank (2) with LH₂ (10) via an inlet (2g), whilst allowing hydrogen boil-off-gas (BOG; 20) generated during the feeding to leave the first storage tank (2) via an outlet (2h);
- (iii) closing the outlet (2h) for hydrogen BOG (20);
- (iv) feeding LHe (40) into the first storage tank (2), in a vapour space (2b) above the liquid level (2c) of the LH₂ (2a) in the first storage tank (2), thereby recondensing hydrogen BOG;
- (v) once the vapour space (2b) has a vapour pressure of below 30 kPag, feeding LHe (30) below a liquid level (2c) of the first storage tank (2) and allowing the LHe to vaporize and bubble through the LH₂ (2a) in the first storage tank (2), preferably forming a cryogenic blanket of helium vapour in the vapour space (2b) above the liquid level (2c) of the LH₂ (2a) in the first storage tank (2).