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A PROCESS FOR CONDENSING A HYDROGEN STREAM

The present invention relates to a process for condensing a hydrogen gas stream, in particular a hydrogen BOG (boil-off gas) stream.

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 liquid hydrogen is the handling of boil-off losses due to the requirement to cool down, heat ingress, the need to depressurize storage tanks, etc. Typically, the boil-off gas flows will be of short duration (in the order of a couple of hours), have a relatively high flow (instantaneous flows of 3 to 4 times the average daily
15 processing rates) and a low frequency (e.g. once a week or once a month).

The above 'intermittent' nature of such boil-off gas flow makes it difficult for e.g. mechanical equipment to deal with. Usually, the intermittent hydrogen BOG is
20 vented.

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)
25 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

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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-absorb and re-process intermittent boil-off gas flows.

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 boil-off gas losses.

It is a further object of the present invention to provide an alternative process for condensing a hydrogen gas stream, in particular a hydrogen BOG stream.

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

- (a) providing a hydrogen gas stream, in particular a hydrogen BOG stream;
- (b) providing a storage tank containing liquid and solid hydrogen (H_2) in co-existence;
- (c) maintaining the co-existence of liquid and solid hydrogen in the storage tank using a heat exchanger;
- (d) feeding the hydrogen gas stream provided in step (a) into the storage tank;
- (e) condensing the hydrogen gas as fed into in the storage tank in step (d).

It has surprisingly been found according to the present invention that by using the cooling capacity of the solid hydrogen, the hydrogen gas (typically a hydrogen BOG stream) as fed into the storage tank in step (d) can be re-condensed in a surprisingly simple manner. As a result, no venting of hydrogen BOG or reprocessing

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thereof outside the tank using (very large) compression systems are needed.

5 A further advantage of the process according to the present invention is that it can reliquefy (very) low pressure streams without the need for mechanical recompression facilities. In addition, since boil-off gas hydrogen will be almost completely in its para-hydrogen spin state, expensive catalytic spin flip will not be required.

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

Typically, the hydrogen gas stream provided in step (a) 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 gas 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.

20 Preferably, the hydrogen gas stream provided in step (a) comprises at least 99.0 wt.% hydrogen, preferably at least 99.999 wt.%, more preferably at least 99.99999 wt.%.
25

Furthermore, it is preferred that the hydrogen gas stream provided in step (a) comprises at least 90 wt.% para-hydrogen, preferably at least 95 wt.%.

30 Although the temperature of the hydrogen gas stream provided in step (a) is not particularly limited, preferably the hydrogen gas stream provided in step (a) has a temperature in the range of 14-60K, preferably below 40K.

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Also, although the pressure of the hydrogen gas stream provided in step (a) is not particularly limited, preferably the hydrogen gas stream provided in step (a) has a pressure in the range of 0.1-5.0 bara, preferably at most 2.0 bara.

In step (b) of the process according to the present invention, a storage tank is provided containing liquid and solid hydrogen (H₂) in co-existence.

As the person skilled in the art will readily understand how to provide a storage tank that contains liquid and solid hydrogen (H₂) in co-existence, this is not further discuss here in detail. Generally, such a storage tank is obtained by partially filling the storage tank with liquid hydrogen. The storage tank is then cooled down (which can take several days or weeks) to such an extent that a substantial amount of liquid hydrogen is converted into solid hydrogen (thereby extracting phase transition energy from the system). As a result, a certain quantity of solid hydrogen or slush hydrogen is formed in the storage tank.

Preferably, the storage tank is operating at a pressure in the range of 0.05-5.0 bara, preferably at most 2.0 bara.

Preferably, the storage tank in step (b) contains a solid hydrogen fraction of at least 20 wt.%, preferably at least 25 wt.%, more preferably at least 30 wt.%, based on the combined amount of liquid and solid hydrogen in the storage tank.

It is in particular preferred that in step (b) the storage tank comprises an amount of solid hydrogen that is at least 2 times, preferably at least 4 times, more preferably at least 8 times the amount of the hydrogen gas stream that is fed into the storage tank in step (d).

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Also, it is preferred that the storage tank provided in step (b) has a cooling capacity of least 1 time, preferably at least 1.5 times, more preferably at least 2 times, of the capacity required to condense the hydrogen gas as fed in step (d).

In step (c) of the process according to the present invention, the co-existence of liquid and solid hydrogen in the storage tank is maintained using a heat exchanger. Typically, this is done using an internal heat exchanger, which can be (and usually is) connected to an external (helium) cooling cycle containing a cryocooler.

In step (d) of the process according to the present invention, the hydrogen gas stream provided in step (a) is fed into the storage tank.

Preferably, the hydrogen gas stream being fed into the storage tank in step (d) has a flow rate that corresponds to at least 10 wt.%, preferably at least 25 wt.% of the solid hydrogen present in the storage tank per hour.

Further, it is preferred that the hydrogen gas is fed via the bottom side of the storage tank and below the fluid level of the solid and liquid hydrogen in the storage tank to allow intimate contact with the solid hydrogen.

In step (e) of the process according to the present invention, the hydrogen gas as fed into the storage tank in step (d) is condensed, by using the available cooling capacity of the solid hydrogen.

In another aspect, the present invention provides an apparatus suitable for performing the process for condensing hydrogen according to the present invention, the apparatus at least comprising:

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- a storage tank containing liquid and solid hydrogen (H₂) in co-existence;

- a heat exchanger placed in the storage tank;

5 wherein the storage tank has an inlet for a hydrogen gas stream.

Preferably, the heat exchanger is connected to an external cryocooler, as part of a cooling cycle.

Further it is preferred that the inlet is connected to a gas distributor placed inside the storage tank.

10 Preferably, the gas distributor can distribute gas below the fluid level of the liquid and solid hydrogen in the storage tank.

Hereinafter the present invention will be further illustrated by the following non-limiting drawings.

15 Herein shows:

Fig. 1 schematically a flow scheme of the process for condensing hydrogen according to the present invention.

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

20 The flow scheme of Figure 1 generally referred to with reference number 1, shows a hydrogen storage tank 2 containing liquid and solid hydrogen in co-existence (in the form of hydrogen slush 3), an internal heat exchanger 4 and an external (helium) cooling cycle containing a
25 cryocooler 5.

During use, a hydrogen gas stream (preferably a hydrogen BOG stream) 10 is provided and fed via inlet 21 into the storage tank 2, which storage tank 2 contains slush hydrogen 3. Typically, the hydrogen gas stream 10
30 is fed in an intermittent manner, i.e. the boil-off gas flows will be of short duration (in the order of a couple of hours), have a relatively high flow (instantaneous

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flows of 3 to 4 times the average daily processing rates) and a low frequency (e.g. once a week or once a month).

5 The co-existence of liquid and solid hydrogen in the storage tank 2 is maintained using the heat exchanger 4 which is connected to the external cryocooler 5.

10 In the embodiment of Fig. 1, the hydrogen gas stream 10 is fed into the storage tank 2 via inlet 21 which is situated at the bottom of the storage tank 2. A gas distributor 6 distributes the gaseous hydrogen below the fluid level of slush hydrogen 3 in the storage tank 2 and ensures intimate contacting of the hydrogen gas with the slush hydrogen 3. As a result, and by using the available cooling capacity of the solid hydrogen, the hydrogen gas as fed into in the storage tank 2 is condensed.

15 Further shown in Fig. 1 is an outlet 22 for liquid hydrogen (LH2) 20, which can be used for removing LH2 20 once desired.

Discussion

20 As can be seen from Fig. 1, the process according to the present invention allows for a surprisingly simple and effective way of condensing a hydrogen stream, in particular a hydrogen BOG stream.

25 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.

30 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

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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.

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C L A I M S

1. A process for condensing a hydrogen gas stream (10),
in particular a hydrogen BOG (boil-off gas) stream, the
process at least comprising the steps of:

- 5 (a) providing a hydrogen gas stream (10), in
particular a hydrogen BOG stream;
- (b) providing a storage tank (2) containing liquid
and solid hydrogen (H_2) in co-existence (3);
- (c) maintaining the co-existence of liquid and solid
10 hydrogen in the storage tank (2) using a heat exchanger
(4);
- (d) feeding the hydrogen gas stream (10) provided in
step (a) into the storage tank (2);
- (e) condensing the hydrogen gas (10) as fed into in
the storage tank (2) in step (d).
- 15 2. The process according to claim 1, wherein the
hydrogen gas stream (10) provided in step (a) comprises
at least 99.0 wt.% hydrogen, preferably at least 99.999
wt.%, more preferably at least 99.99999 wt.%.
- 20 3. The process according to claim 1 or 2, wherein the
hydrogen gas stream (10) provided in step (a) comprises
at least 90 wt.% para-hydrogen, preferably at least 95
wt.%.
- 25 4. The process according to any one of the preceding
claims, wherein the hydrogen gas stream (10) provided in
step (a) has a temperature in the range of 14-60K,
preferably below 40K.
- 30 5. The process according to any one of the preceding
claims, wherein the hydrogen gas stream provided (10) in
step (a) has a pressure in the range of 0.1-5.0 bara,
preferably at most 2.0 bara.

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6. The process according to any one of the preceding claims, wherein the storage tank (2) is operating at a pressure in the range of 0.05-5.0 bara, preferably at most 2.0 bara.

5 7. The process according to any one of the preceding claims, wherein in step (b) the storage tank (2) comprises an amount of solid hydrogen that is at least 2 times, preferably at least 4 times, more preferably at least 8 times the amount of the hydrogen gas stream (10) that is fed into the storage tank (2) in step (d).

10 8. The process according to any one of the preceding claims, wherein the storage tank (2) provided in step (b) has a cooling capacity of at least 1 time, preferably at least 1.5 times, more preferably at least 2 times, of the capacity required to condense the hydrogen gas as fed in step (d).

15 9. The process according to any one of the preceding claims, wherein the hydrogen gas stream (10) being fed into the storage tank (2) in step (d) has a flow rate that corresponds to at least 10 wt.%, preferably at least 20 25 wt.% of the solid hydrogen present in the storage tank per hour.

25 10. An apparatus (1) suitable for performing the process for condensing hydrogen according to any one of the preceding claims 1-9, the apparatus (1) at least comprising:

30 - a storage tank (2) containing liquid and solid hydrogen (H_2) in co-existence (3);
- a heat exchanger (4) placed in the storage tank (2);

wherein the storage tank (2) has an inlet (21) for a hydrogen gas stream (10) to be re-condensed.

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11. Apparatus (1) according to claim 10, wherein the heat exchanger (4) is connected to an external cryocooler (5).
12. Apparatus (1) according to claim 10 or 11, wherein
5 the inlet (21) is connected to a gas distributor (6) placed inside the storage tank (2).