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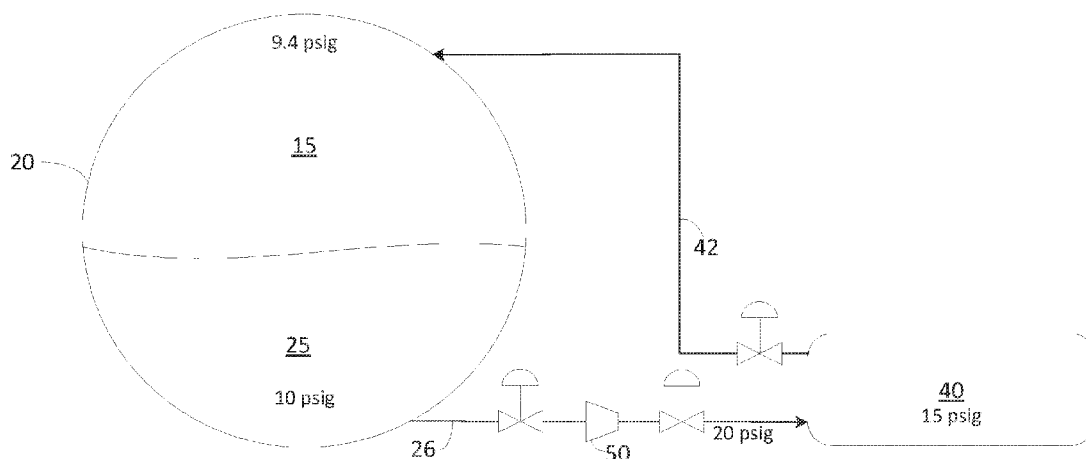
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(54) Title: ARCHITECTURE FOR LOADING LIQUID HYDROGEN TRAILERS

FIG. 6



(57) Abstract: A method for filling a hydrogen delivery trailer (40) is provided, in which the method can include the steps of: transferring liquid hydrogen from a liquid hydrogen storage vessel (20, 80) to the hydrogen delivery trailer (40) via a liquid transfer line (26); and sending gaseous hydrogen from a gas headspace (15) of the hydrogen delivery trailer (40) to the liquid hydrogen storage vessel (20) via a gaseous transfer line (42), wherein the liquid hydrogen storage vessel (20) is configured to be in fluid communication with a hydrogen liquefier, such that the liquid hydrogen storage vessel (20) is configured to receive liquid hydrogen from the hydrogen liquefier.



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ARCHITECTURE FOR LOADING LIQUID HYDROGEN TRAILERS

Cross Reference of Related Applications

- 5 This patent application claims priority to U.S. Provisional Patent Application Serial No. 63/523,537 filed on June 27, 2023, which is hereby incorporated by reference in its entirety.

Background of the Invention

Liquid hydrogen trailer loading is a lengthy process that also leads to significant hydrogen venting. Liquid hydrogen trailers arrive at the liquefier with a significant amount of hydrogen
10 gas that must be managed. In order to fill a trailer with hydrogen, the gaseous hydrogen in the trailer is often removed until the trailer is at a low pressure, commonly referred to as depressurization. The trailer then enters the loading phase.

While the trailer is “empty,” there is a small amount of liquid hydrogen within the trailer and a large volume of gaseous hydrogen within the trailer. The gaseous hydrogen should be
15 removed so that liquid can fill the trailer. In addition, the flow coming into the trailer typically contains a fraction of gas hydrogen because 1) some heat is absorbed in the piping that vaporizes liquid hydrogen to gas hydrogen and 2) the incoming flow was saturated at a pressure higher than the trailer pressure which causes the liquid stream to flash to a two phase fluid (liquid and gas). The gas created from cooling down the piping and from flashing should be
20 removed from the trailer to allow the trailer to fill with additional liquid hydrogen.

The amount of gas and the rate of gas formation varies, and in order to depressurize and load the trailer as quickly as possible, the gas should be removed as soon as it is available. If the gas is not removed when it is available, the step takes longer than needed.

For example, during depressurization, a large amount of hydrogen gas (~200 kg) is immediately available to be removed from the trailer, and a slow flow rate of hydrogen gas being removed from the trailer will increase the duration of this activity. During loading, the hydrogen gas from the vapor space and the hydrogen gas produced from piping cooldown and
5 flashing can fill the trailer gas space and cause the pressure in the trailer to increase. The increased pressure in the trailer slows the flow of liquid hydrogen from the liquid hydrogen storage vessel and increases the duration of the loading step.

The current methods for removing the gas from the trailer are 1) by venting the gas from the trailer to atmosphere, or 2) by compressing the gas from the trailer to a higher pressure so that
10 the gas can be used in the liquefier process. Venting the gas to atmosphere allows the gas to be removed from the trailer at a very high flow rate (basically as soon as it the gas is available), and the pressure in the trailer is maintained at near atmospheric pressure. Compressing the gas from the trailer to a higher pressure occurs at a fixed flow rate of the compressor, and the pressure in the trailer is elevated up to ~5 psig in order to have sufficient pressure supply the
15 compressor suction. Compressing the gas limits the flow rate of gas that can be removed from the trailer, and this limited flow rate slows the trailer depressurization and loading process.

Another factor that impacts the speed of trailer filling is the pressure drop that is available between the liquid hydrogen storage vessel and the trailer. After depressurization and when excess gas from loading has been removed from the trailer, the pressure drop available
20 determines the flow rate of liquid hydrogen from the liquid hydrogen storage vessel to the trailer. Given that the piping system has a fixed resistance and the outlet conditions of the liquid hydrogen storage vessel are constant, the pressure drop correlates to the flow rate of liquid hydrogen from the liquid hydrogen storage vessel to the trailer. In order to load trailers more quickly, the pressure drop from the liquid hydrogen storage vessel to the trailer should be

maximized. Liquid hydrogen storage vessels are typically maintained around 10-20 psig. The pressure drop available depends on the method used to remove gas from a trailer. When a compressor is used to remove gas from a trailer, the pressure drop available is 5-15 psi (10-20 psig minus 5 psig). When the trailer gas is removed by a vent, the pressure drop available is 10-20 psi. Trailers typically carry about 4,000 kg, and the liquid hydrogen flow rate from the liquid hydrogen storage vessel to the trailer is shown below:

Table I: Liquid Hydrogen Flow Rates

Vapor destination	Fill rate
Vent	~25 kg/min
Compressor	~15 kg/min
Compressor + vent	~15 kg/min

The liquid hydrogen transfer duration can be 2.5 – 4.5 hours, this does not include hose connection, valve manipulations, and purging/cooldown sequences. The total time required to fill a trailer consists of depressurization and loading, so the total duration is typically closer to about 6 hours.

A solution is needed to improve the duration to depressurize and to load a trailer while recovering all of the gas into the liquefier.

A larger compressor would allow gas to be recovered, but this compressor would not improve the duration for loading a trailer (same pressure drop available) and would not improve the duration for depressurization as compared to venting during depressurization. In addition, compressors that have high flow rates and low suction pressures are prohibitively expensive; a compressor larger than the current compressor sizing is not economically justifiable.

The combination of a liquid pump and a gas compressor could load trailers quickly and avoid wasting the hydrogen gas from the trailer; however, the compressor CAPEX would need to be even larger than the compressor used for recovering more gas hydrogen because the pump causes a large liquid hydrogen flow rate that requires a very high flow rate of gas hydrogen to
5 be removed from the trailer by the compressor. Also the centrifugal liquid hydrogen pump is a relatively unproven component, and there are not any proven liquid hydrogen pumps that can operate with very low NPSH (condition of the liquid hydrogen storage vessel).

In general, the current state of the art has the following problems:

- Hydrogen vented to the atmosphere is wasted instead of being recovered, thereby
10 causing a loss of value, increased global warming impact, and heightened safety concerns from venting large amounts of hydrogen.
- Slow loading results in significant man-hours to oversee the long loading, and due to the slow loading, many loading bays are needed to meet the liquefier's production capacity, thereby further increasing the capital investment of liquid hydrogen
15 production.

Solutions are limited due to high CAPEX of compressors, and no proven liquid hydrogen pumps that operate with very low net positive suction head (NPSH).

Summary of the Invention

As noted above, the low-pressure, recycle hydrogen compressor for recovery of the boil-off
20 gas (BOG) is not sized to properly handle the large volume of flow of the gaseous hydrogen coming from the trailers during refilling. To size the compressor properly for the instantaneous flow rates, it would be far too expensive and would not be running at its most efficient rate during the majority of the day.

In certain embodiments, the invention allows for rapid depressurization and rapid loading of trailers while recovering the gas hydrogen from the trailer. In certain embodiments, the invention allows gas hydrogen from the trailer to be removed to a large vessel (or grouping of vessels) that can store the gas hydrogen. This storage volume allows for removal of the
5 hydrogen gas from the trailer as soon as the hydrogen gas is available. Next, a pump is used to transfer liquid hydrogen at large flow rates (~75 kg/min). In certain embodiments, the gas hydrogen from the trailer pressurizes a liquid hydrogen storage vessel, which provides NPSH for a pump to transfer liquid hydrogen at large flow rates. The gas hydrogen in the storage vessel causes the pressure in the storage vessel to increase, and the pressure in the storage
10 vessel can be managed by venting, by compressing the gas to a higher pressure, or by liquefying the gas hydrogen to liquid hydrogen

In certain embodiments, the present invention may use an existing liquid hydrogen storage container as a pseudo-buffer tank for the gaseous hydrogen coming from the trailers during refill. In an alternative embodiment, a separate gaseous hydrogen storage tank could also be
15 used; however, it is less preferred from a CAPEX standpoint. Additionally, this alternative embodiment would increase operation expenditures (OPEX) as well, since it does not advantageously help with building up the head pressure of the liquid hydrogen storage tank during refill.

In certain embodiments, this gaseous hydrogen may be temporarily stored in the liquid
20 hydrogen storage tank during filling, and then can be recycled back to the liquefier feed using the typical low-pressure boil-off gas (BOG) compressor. The hydrogen gas from the trailer can be removed from the trailer as soon as the gas is available. Meanwhile the compressor only has to be sized for the average flow rate of the gas removal because the liquid hydrogen storage tank serves as a buffer for the instantaneous flow rates. This sizing technique for the compressor

allows the compressor to be much smaller than the compressor required for the instantaneous flow rates of hydrogen gas that needs to be removed from the liquid hydrogen trailer.

In another embodiment, the gaseous hydrogen may be condensed within the liquid hydrogen storage tank using subcooled liquid hydrogen from the liquefier or having a condenser in the headspace. In certain embodiments, the refrigerant flowing through the condenser may comprise helium.

In another embodiment, instead of one large liquid hydrogen sphere, a parallel grouping of bullet tanks may be employed. Each tank would be volumetrically smaller than a single storage sphere, which means that their pressure could be increased more easily (i.e., same amount of gaseous hydrogen going from the delivery tank makes a bigger difference with a smaller liquid hydrogen tank).

In short, certain embodiments of the invention may provide the benefits of: recovering additional gaseous hydrogen molecules, recovering frigories of the gaseous hydrogen molecules, and improved filling times (e.g., possibly 4x).

In certain embodiments of the invention, a method for filling a hydrogen delivery trailer is provided. In this embodiment, the method may include the steps of: transferring liquid hydrogen from a liquid hydrogen storage vessel to the hydrogen delivery trailer via a liquid transfer line; and sending gaseous hydrogen from a gas headspace of the hydrogen delivery trailer to the liquid hydrogen storage vessel via a gaseous transfer line, wherein the liquid hydrogen storage vessel is configured to be in fluid communication with a hydrogen liquefier, such that the liquid hydrogen storage vessel is configured to receive liquid hydrogen from the hydrogen liquefier.

In optional embodiments of the method for filling the hydrogen delivery trailer:

- the method can further include a step of c) treating the gaseous hydrogen of the liquid hydrogen storage vessel;
- step c) comprises sending the gaseous hydrogen to the hydrogen liquefier for
5 liquefaction therein;
- step c) further comprises liquefying the gaseous hydrogen of the liquid hydrogen storage vessel;
- the gaseous hydrogen is liquefied using cooling provided by a refrigeration cycle having a refrigerant;
- 10 • the cooling takes place within the headspace of the liquid hydrogen storage vessel or outside of the liquid hydrogen storage vessel;
- the refrigerant is configured to provide cooling to 20K to 22K;
- the refrigerant is selected from the group consisting of helium, hydrogen, neon, and combinations thereof;
- 15 • the gaseous hydrogen is liquefied by introducing a subcooled liquid hydrogen stream through the headspace, thereby providing direct contact with the gaseous hydrogen;
- the subcooled liquid hydrogen stream is introduced using a spray header;
- the gaseous hydrogen is liquefied by indirect heat exchange via a top condenser that is cooled using a refrigerant;
- 20 • the refrigerant is configured to provide cooling to 20K to 22K;
- the refrigerant is selected from the group consisting of helium, hydrogen, neon, and combinations thereof;
- the gaseous hydrogen is liquefied by sending the gaseous hydrogen to the hydrogen liquefier as boil-off gas from the liquid hydrogen storage vessel;
- 25 • step 0 includes the use of a liquid pump disposed on the liquid transfer line;

- the liquid hydrogen storage vessel comprises a spherical tank;
- the liquid hydrogen storage vessel comprises a plurality of bullet tanks;
- step a) further comprises the steps of:
 - selecting a first bullet tank of the plurality of bullet tanks that has the
 - 5 highest gas phase pressure;
 - equalizing the pressure of the gas phase of the first bullet tank and the hydrogen delivery trailer; and
 - pumping liquid hydrogen from the first bullet tank to the hydrogen delivery trailer until the hydrogen delivery trailer reaches a predetermined value;
 - 10 • the method can further include the steps of:
 - stopping fluid communication between the first bullet tank and the hydrogen delivery trailer;
 - selecting a second bullet tank of the plurality of bullet tanks that has the second highest gas phase pressure;
 - 15 ○ equalizing the pressure of the gas phase of the second bullet tank and the hydrogen delivery trailer; and
 - pumping liquid hydrogen from the second bullet tank to the hydrogen delivery trailer until the hydrogen delivery trailer reaches a second predetermined value; and/or
 - 20 • the method can further include a step of c) treating the gaseous hydrogen of the liquid hydrogen storage vessel, wherein step c) further comprises sending gaseous hydrogen from the plurality of bullet tanks to the hydrogen liquefier for liquefaction therein.

Brief Description of the Drawings

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, claims, and accompanying drawings. It is to be noted, however, that the drawings illustrate only several embodiments of the invention and are therefore not to be considered limiting of the invention's scope as it can admit to other equally effective embodiments.

FIG. 1 shows an embodiment of the invention.

FIG. 2 shows a second embodiment of the invention.

FIG. 3 provides a third embodiment of the invention.

FIG. 4 provides an embodiment of the prior art.

FIG. 5 provides a fourth embodiment of the present invention.

FIG. 6 provides a fifth embodiment of the present invention.

FIG. 7 provides a sixth embodiment of the present invention.

Detailed Description

While the invention will be described in connection with several embodiments, it will be understood that it is not intended to limit the invention to those embodiments. On the contrary, it is intended to cover all the alternatives, modifications and equivalence as may be included within the spirit and scope of the invention defined by the appended claims.

In no particular order, certain embodiments of the invention aim to:

- 1) store the gaseous hydrogen returning from the trailer;
- 2) liquefy the gaseous hydrogen into liquid hydrogen; and

- 3) increase the flow rate of liquid hydrogen to the trailer

Storage of the gaseous hydrogen

Gaseous hydrogen is present in the trailer when it returns to the liquefier, and gaseous hydrogen is created when heat enters the system. Furthermore, a small amount of gaseous hydrogen is always being created in the liquid hydrogen storage container. When the trailer depressurization occurs, there is a large amount of gaseous hydrogen (up to 200 kg) that needs to be removed from the trailer. In order to remove the gaseous hydrogen quickly, the plant often vents the gaseous hydrogen to atmosphere because recovery of the gaseous hydrogen from the trailer is a lengthy process. Also, there is a substantial amount of gaseous hydrogen that needs to be removed from the trailer during loading, and this gaseous hydrogen creates the same dilemma.

Venting can be reduced by having a dedicated low-pressure storage for this hydrogen that was otherwise vented, which can accept the large instantaneous flow rates of gaseous hydrogen, and then the hydrogen can be processed over a longer period of time. However, this solution suffers from requiring a larger footprint, increased CAPEX (for the extra storage vessel), and it also fails to recover any of the frigories from the gaseous hydrogen.

In a first embodiment, the gaseous hydrogen can be recovered into the headspace of an existing cold liquid hydrogen storage container. The gas line for this will preferably be insulated throughout the system to ensure that little heat is added back to the liquid hydrogen storage container. The molecules and the refrigeration power of the gaseous hydrogen is recovered in this process.

This embodiment has the benefit of utilizing an existing liquid hydrogen storage container, thereby reducing CAPEX expenditures as compared to existing solutions. Additionally, the headspace of the existing liquid hydrogen storage container typically has a substantial volume, thereby allowing for the ability to handle the large volumetric flows from incoming trailers.

5 Moreover, the headspace of the liquid hydrogen storage container is cold, and therefore, it will keep the gaseous hydrogen in its cold state, which requires much less volume than storing the gaseous hydrogen at ambient temperatures. Lastly, the gaseous hydrogen will interact with the liquid hydrogen to form a new equilibrium, which will result in some of the gaseous hydrogen to condense, thereby causing the pressure to decrease.

10 In alternative embodiments of the present invention:

- the gaseous hydrogen recovered may enter the top or the bottom of the liquid hydrogen storage container to better control pressure in the liquid hydrogen storage container;
 - in the case of multiple liquid hydrogen storage containers, the gaseous hydrogen may also be able to be directed to the top or bottom of a separate liquid hydrogen storage
- 15 container from the one that is supplying liquid hydrogen to the trailer.

Conversion to liquid hydrogen

Following storage of the gaseous hydrogen from the trailer to the liquid hydrogen storage container, the gaseous hydrogen may then be liquefied. In addition to the gaseous hydrogen recovered from the trailer, the liquid hydrogen storage container will be creating continuous

20 boil-off gaseous hydrogen that also needs to be liquefied. With the gaseous hydrogen in a storage container, the liquefaction can occur at a steady flow rate (Steady flow rate = the average flow rate instead of the instantaneous flow rate from the trailers). Adding gaseous hydrogen to the liquefaction process at a constant flow rate is much more manageable for the control of the liquefaction process.

In certain embodiments, the gaseous hydrogen may be converted to liquid hydrogen by compressing low-pressure gaseous hydrogen (~5 psig) to a higher pressure (>300 psig) and injecting it into the gaseous hydrogen feed circuit of the liquefier where it will be liquefied to liquid hydrogen. This process is sufficient, but has the problems listed below:

- 5 • CAPEX of the compressor
 - OPEX of the compressor
 - poor reliability of rotating equipment
 - increased maintenance of rotating equipment
 - increased process complexity
- 10 Hydrogen is commonly liquefied by a nitrogen refrigeration loop to cool the hydrogen to 80K and either a hydrogen refrigeration loop or a helium refrigeration loop to cool the hydrogen to 25K. Hydrogen product may be introduced to the liquefier at elevated pressures (~300 psig), and the hydrogen product remains at high pressures during the cooling steps. After the final cooling step, the hydrogen is expanded across a valve or a turbine to reach the final state of
- 15 liquid hydrogen at low pressures (~10 psig). Certain embodiments of the present invention seek to utilize at least some of this existing infrastructure in order to liquefy the low-pressure gaseous hydrogen originating from the trailer.

In another embodiment, which is shown in FIG. 1, subcooled liquid hydrogen 2 may be introduced through a spray header 10, which allows for improved contact between the

20 subcooled droplets 12 and gaseous hydrogen 15 within the headspace of the storage tank 20. The colder liquid hydrogen will interact with the gaseous hydrogen and cause some of the gaseous hydrogen to condense. This process liquefies the gaseous hydrogen into liquid hydrogen 25 directly in the storage sphere. This embodiment is beneficial since it does not require specialized equipment such as a compressor or a flash drum. Moreover, this

embodiment allows for a reduction in the sizing and complexity of many, if not all, heat exchangers, since there is no need for a path for the gaseous hydrogen to travel from the cold side to the warm side of the process.

In one embodiment, a solution to liquefy the low-pressure gaseous hydrogen is to condense the
5 gaseous hydrogen into liquid hydrogen within the existing liquid hydrogen storage container. This may be achieved, for example, by condensing gaseous hydrogen into liquid hydrogen through the use of a low temperature refrigeration cycle. As shown in FIG. 2, gaseous hydrogen from headspace 15 may be withdrawn via conduit 34 and then introduced into heat exchanger 230, wherein it is liquefied against the refrigerant that flows through conduits 228
10 and 232. The now liquefied hydrogen 234 can then be returned back to the liquid hydrogen storage vessel 20.

In an optional embodiment, a gaseous withdrawal line 36 can be used to send gaseous hydrogen to the hydrogen liquefier. As this flow rate can be managed independently of the filling of the transport trailers, this embodiment allows increased flexibility in handling the large gaseous
15 flows, all without adding any significant equipment to the hydrogen liquefier (i.e., no extra compressors, heat exchangers, etc...)

In certain embodiments, the refrigerant used as part of the refrigeration cycle can include one or more of helium, neon, and hydrogen.

In another embodiment, which is shown in FIG. 3, a condenser 30 may be provided within the
20 headspace 15 the liquid hydrogen storage container 20. The condenser may be filled with a cold liquid refrigerant 28 (preferably at around 21K), and as the refrigerant absorbs heat by condensing the gaseous hydrogen, the refrigerant will vaporize and be returned 32 to its

refrigeration cycle. In certain embodiments, the refrigerant can include one or more of helium, neon, and hydrogen.

The benefits of this embodiment include:

- the hydrogen refrigeration cycle already includes a low suction pressure refrigerant compressor;
- simplify the process by not introducing more flow into the 20K coldbox; and
- the liquefaction of gaseous hydrogen does not have to occur at the instantaneous flow rate of gaseous hydrogen because the pressure in the sphere can increase to store additional gaseous hydrogen.

10 Increase flow rate of liquid hydrogen to the trailer

Liquid hydrogen flows from the liquid hydrogen storage tank 20 (e.g., sphere) to the trailer 40 due to a pressure gradient. This pressure gradient and the characteristic resistance of the piping system (fixed) determine the flow rate of liquid hydrogen into the trailer. Normally, the pressure gradient is provided by holding the sphere at a higher pressure and either venting the gas 41 in the trailer 40 to the atmosphere or recovering the gas into the suction of a low-pressure compressor.

As an example, the pressure of the sphere may be around 10 psig, with the trailer having a pressure of approximately 5 psig. When venting the hydrogen gas to the atmosphere, atmospheric pressure is 0 psig, which allows for approximately 20 kg/min liquid hydrogen to flow into the trailer. When sending the gaseous hydrogen to a low-pressure compressor, its pressure is around 6 psig, which significantly reduces the flow of liquid hydrogen to the trailer to around 10 kg/min. The pressure gradient during the trailer filling for this example is shown in FIG 4.

FIG. 5 provides for an alternate embodiment to FIG. 4; however, the embodiment shown in FIG. 5 still is not ideal, since the pressure gradient is still too small, thereby resulting in a low liquid hydrogen flow rate. For example, assuming the same characteristic resistance of the circuit, the flow rate would be <5 kg/min, and the trailer loading would take much too long.

- 5 FIG. 6 provides a solution to alleviate this problem. For example, a liquid pump 50 may be provided between the sphere 20 and the trailer 40 in order to pressurize the liquid hydrogen 26 coming from the sphere to a higher pressure (e.g., 20 psig). This would provide an acceptable pressure gradient to force the gaseous hydrogen 42 out of the trailer and into the headspace 15 of the sphere 20, thereby increasing the overall flow rate of liquid hydrogen into the trailer 40.
- 10 For example, the flow rate to load a trailer could easily be $60+$ kg/min in this configuration, which will shorten loading times to approximately 33% of the current loading time.

Centrifugal pumps

- There are a limited number of industrial liquid hydrogen centrifugal pumps that have proven reliability when working with hydrogen. Further, no liquid hydrogen centrifugal pumps are
- 15 designed to run with extremely low net positive suction head (NPSH) (< 5 psi), which is currently the condition of the liquid hydrogen storage container.

- A minimum level of NPSH is needed to pump the liquid. Current liquid hydrogen pumps are designed for a minimum available NPSHa of 5 psi with significant margin, which is why a
- 20 simple addition of a liquid pump to the embodiment of FIG. 5 is unsatisfactory.

Therefore, embodiments of the present invention overcome the NPSHa issue by redirecting the gaseous hydrogen from the trailer into an existing liquid hydrogen storage vessel (e.g., sphere or bullet tanks). By managing the trailer loading process with specific control of the gaseous

hydrogen that is in the trailer, the pressure within the liquid hydrogen storage vessel will increase, which in turn provides a sufficient NPSH for a liquid hydrogen centrifugal pump.

Liquid hydrogen storage

Large onsite storage is needed at liquefiers to hold inventory for downtime (e.g., maintenance activities, high utility costs, etc.). The storage is commonly a large sphere or multiple bullet vessels. Bullet vessels are horizontal or vertical storage vessels that are able to be transported from the place of manufacture to the site of the liquefier. A large spherical liquid hydrogen storage container must be constructed onsite, which has a very long duration and high cost. Due to the advantages of the bullet tanks, liquefier suppliers are often providing bullet tanks for the liquid hydrogen storage.

As an aside, a person of ordinary skill will recognize that, while FIGs. 1-6 all show the use of a spherical liquid hydrogen tank, the embodiments of those figures should not be limited to large spheres. Rather, a plurality of bullet tanks may also be used with the embodiments shown in FIGs. 1-6, and in particular FIG. 2

For example, in another embodiment of the present invention, the solution may include storage with multiple bullet tanks because the proportion of volume in the trailer is closer to the volume of one bullet tank. As shown in FIG 7, separate valves to the gas side 75 and the liquid hydrogen side 70 of each bullet tank 80A, 80B, 80C can be employed so that the fill bay can have access to the gas phase and the liquid phase of any individual bullet tank.

In an embodiment incorporating a set of bullet tanks, the following steps may be employed:

- prior to loading the trailer, equalize between the gas phase of the bullet tank and the trailer;
- pump from the bullet tank to the trailer until the trailer is full;

- connect the trailer gas space to the gas space of the next highest pressure liquid hydrogen storage container. (if there are multiple liquid hydrogen storage containers);
 - continue until the trailer gas space has been opened to the gas space of the liquid hydrogen container with the lowest pressure. (if there are multiple liquid hydrogen storage containers); and
 - remove the gaseous hydrogen from each of the bullet tanks to return to the bullet tank to the original low pressure by liquefying the low pressure gaseous hydrogen in the liquid hydrogen storage container (Solutions 2 and 3), by removing the gaseous hydrogen with a compressor, or by venting the gaseous hydrogen.
- 10 The use of the embodiments shown in FIGs. 5 and 6 allow the ability to run a centrifugal pump by supplying the NPSH required for the pump. In additional embodiments, the bullet tank setup can have the following alterations:
- the bullet tanks could be placed at varying heights. The lower vessel will always have more liquid hydrogen and less gas space, which creates a better condition for building
- 15 NPSHA for the pump;
- after the vapor recovery, the bullet tanks can all be equalized or the vapor can be removed from an individual bullet tank;
 - the solution can also be used with a sphere, but with less impact on NPSH.
 - connecting one trailer directly to a single bullet vessel (See Attachment 2 for
- 20 steps).

As discussed herein, embodiments of the present invention advantageously allow for 1) storing gaseous hydrogen, 2) liquefying gaseous hydrogen at low pressure, and 3) providing NPSH to allow pumping via existing centrifugal pumps. The resulting overall benefits include: lower CAPEX (less fill bays, no extra gas compressors, no dedicated gas storage container), recovery

of gaseous hydrogen molecules (increased efficiency); faster filling of liquid hydrogen trailers; and simplification of the plant/process design.

While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims. The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. Furthermore, if there is language referring to order, such as first and second, it should be understood in an exemplary sense and not in a limiting sense. For example, it can be recognized by those skilled in the art that certain steps can be combined into a single step.

The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

"Comprising" in a claim is an open transitional term which means the subsequently identified claim elements are a nonexclusive listing (i.e., anything else may be additionally included and remain within the scope of "comprising"). "Comprising" as used herein may be replaced by the more limited transitional terms "consisting essentially of" and "consisting of" unless otherwise indicated herein.

"Providing" in a claim is defined to mean furnishing, supplying, making available, or preparing something. The step may be performed by any actor in the absence of express language in the claim to the contrary.

Optional or optionally means that the subsequently described event or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

Ranges may be expressed herein as from about one particular value, and/or to about another
5 particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range.

CLAIMS

I claim:

1. A method for filling a hydrogen delivery trailer (40), the method comprising the steps
5 of:
 - a) transferring liquid hydrogen (25) from a liquid hydrogen storage vessel (20, 80) to the hydrogen delivery trailer (40) via a liquid transfer line (26); and
 - b) sending gaseous hydrogen from a gas headspace (15) of the hydrogen delivery trailer (40) to the liquid hydrogen storage vessel (20, 80) via a gaseous transfer line (42),
10 wherein the liquid hydrogen storage vessel (20, 80) is configured to be in fluid communication with a hydrogen liquefier, such that the liquid hydrogen storage vessel (20, 80) is configured to receive liquid hydrogen from the hydrogen liquefier.
2. The method as claimed in Claim 1, further comprising a step of c) treating the gaseous hydrogen of the liquid hydrogen storage vessel (20, 80).
- 15 3. The method as claimed in Claim 2, wherein step c) comprises sending the gaseous hydrogen to the hydrogen liquefier for liquefaction therein.
4. The method as claimed in Claim 3, wherein the gaseous hydrogen is liquefied by sending the gaseous hydrogen to the hydrogen liquefier as boil-off gas from the liquid hydrogen storage vessel (20, 80).
- 20 5. The method as claimed in Claim 2, wherein step c) further comprises liquefying the gaseous hydrogen within the liquid hydrogen storage vessel (20, 80).
6. The method as claimed in Claim 5, wherein the gaseous hydrogen is liquefied using cooling provided by a refrigeration cycle having a refrigerant.

7. The method as claimed in Claim 6, wherein the cooling takes place within the gas headspace (15) of the liquid hydrogen storage vessel (20, 80) or outside of the liquid hydrogen storage vessel (20, 80) using an indirect heat exchanger (230).
8. The method as claimed in Claim 6, wherein the refrigerant is configured to provide
5 cooling to 20K to 22K.
9. The method as claimed in Claim 6, wherein the refrigerant is selected from the group consisting of helium, hydrogen, neon, and combinations thereof.
10. The method as claimed in Claim 5, wherein the gaseous hydrogen is liquefied by introducing a subcooled liquid hydrogen stream (2) through the gas headspace (15), thereby
10 providing direct contact with the gaseous hydrogen.
11. The method as claimed in Claim 10, wherein the subcooled liquid hydrogen stream (2) is introduced using a spray header (10).
12. The method as claimed in Claim 5, wherein the gaseous hydrogen is liquefied by indirect heat exchange via a top condenser (30) that is cooled using a refrigerant.
13. The method as claimed in Claim 12, wherein the refrigerant is configured to provide
15 cooling to 20K to 22K.
14. The method as claimed in Claim 12, wherein the refrigerant is selected from the group consisting of helium, hydrogen, neon, and combinations thereof.
15. The method as claimed in Claim 1, wherein step a) includes the use of a liquid pump
20 (50) disposed on the liquid transfer line (26).

16. The method as claimed in Claim 1, wherein the liquid hydrogen storage vessel (20) comprises a spherical tank (20).
17. The method as claimed in Claim 1, wherein the liquid hydrogen storage vessel (80) comprises a plurality of bullet tanks (80a, 80b, 80c).
- 5 18. The method as claimed in Claim 17, wherein step a) further comprises the steps of:
selecting a first bullet tank (80A) of the plurality of bullet tanks that has the highest gas phase pressure;
equalizing the pressure of the gas phase of the first bullet tank (80A) and the hydrogen delivery trailer (40); and
10 pumping (50) liquid hydrogen from the first bullet tank (80A) to the hydrogen delivery trailer (40) until the hydrogen delivery trailer (40) reaches a predetermined value.
19. The method as claimed in Claim 18, further comprising the steps of:
stopping fluid communication between the first bullet tank (80A) and the hydrogen delivery trailer (40);
15 selecting a second bullet tank (80B) of the plurality of bullet tanks that has the second highest gas phase pressure;
equalizing the pressure of the gas phase of the second bullet tank (80B) and the hydrogen delivery trailer (40); and
pumping (50) liquid hydrogen from the second bullet tank (80B) to the hydrogen
20 delivery trailer (40) until the hydrogen delivery trailer (40) reaches a second predetermined value.
20. The method as claimed in Claim 17, further comprising a step of c) treating the gaseous hydrogen of the liquid hydrogen storage vessel (80a, 80b, 80c), wherein step c) further

comprises sending gaseous hydrogen from the plurality of bullet tanks (80a, 80b, 80c) to the hydrogen liquefier for liquefaction therein.

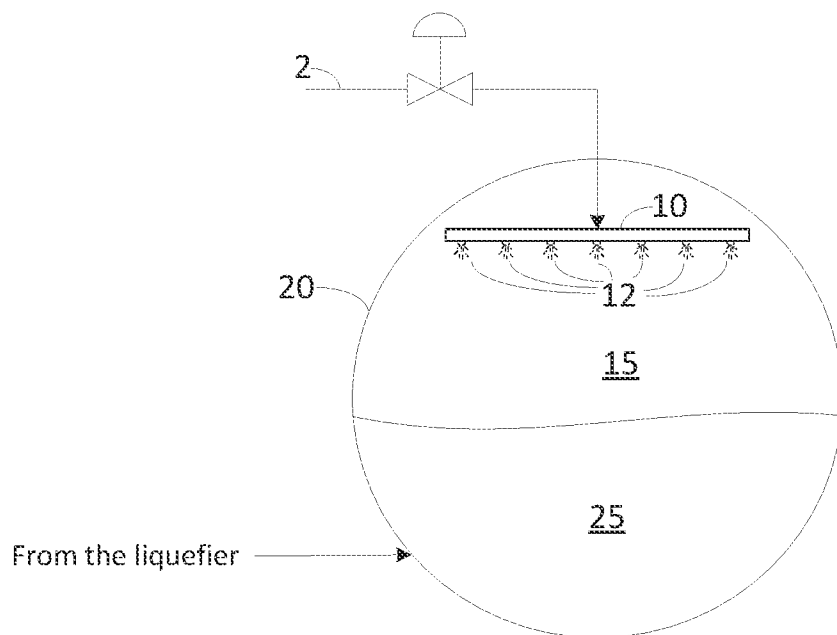


FIG. 1

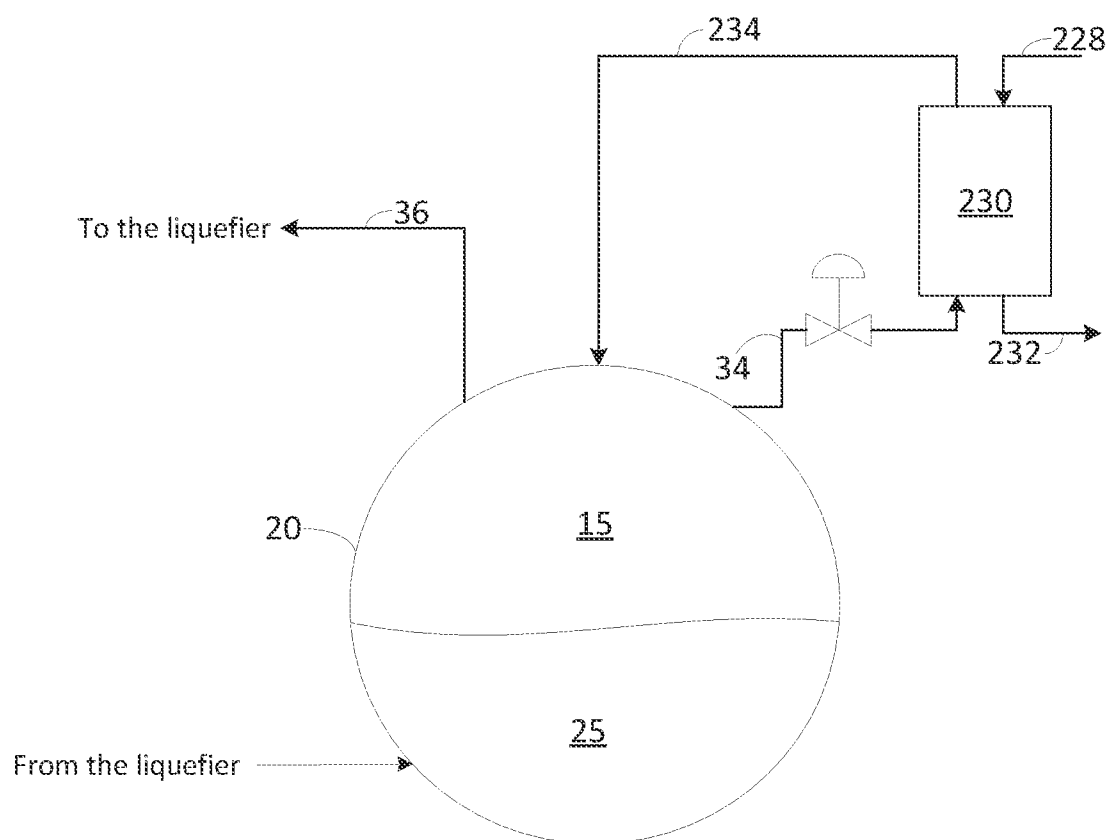


FIG. 2

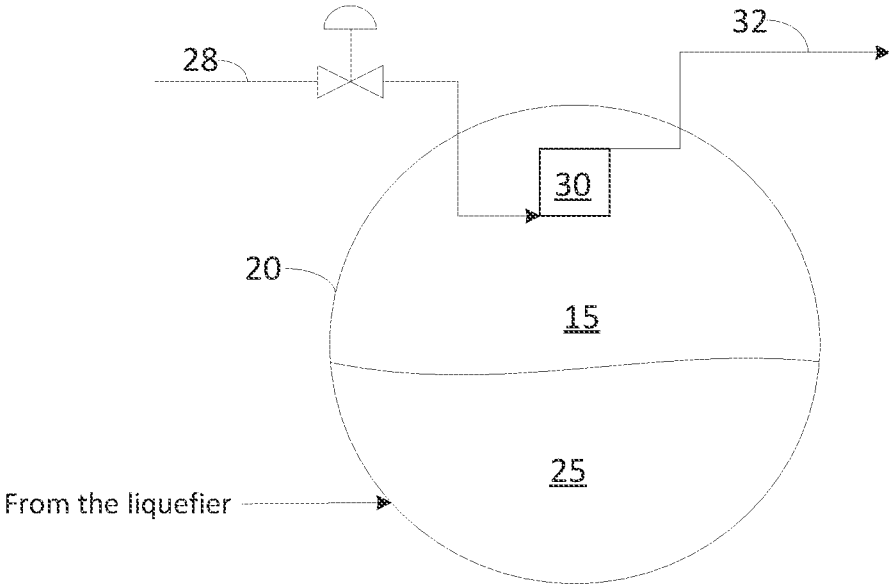


FIG. 3

FIG. 4
(Prior Art)

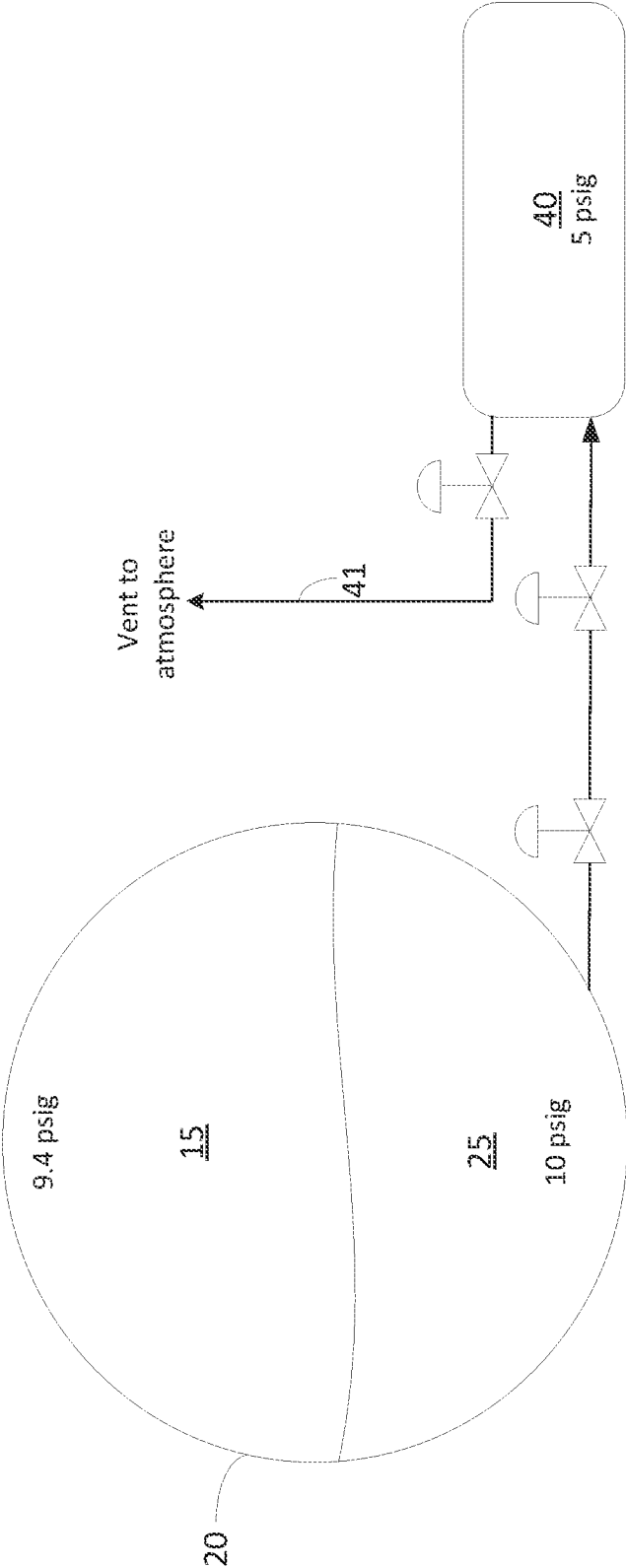


FIG. 5

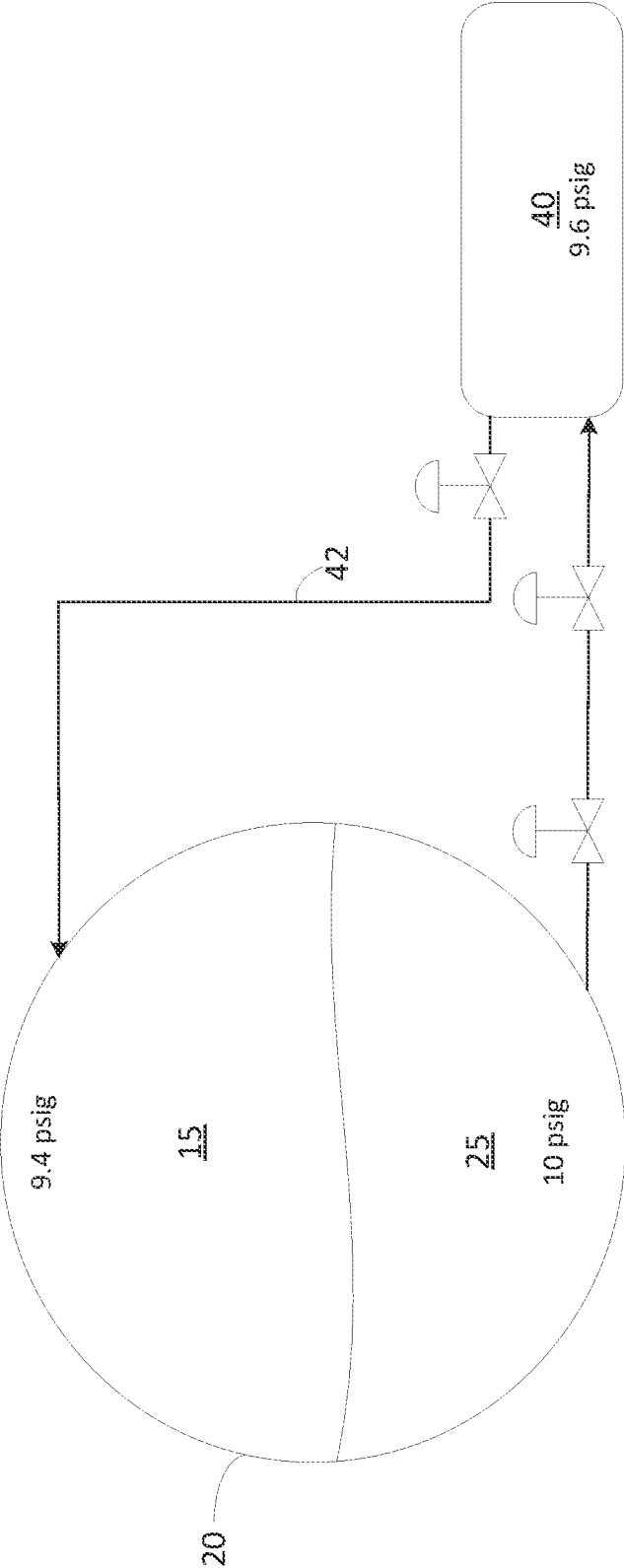


FIG. 6

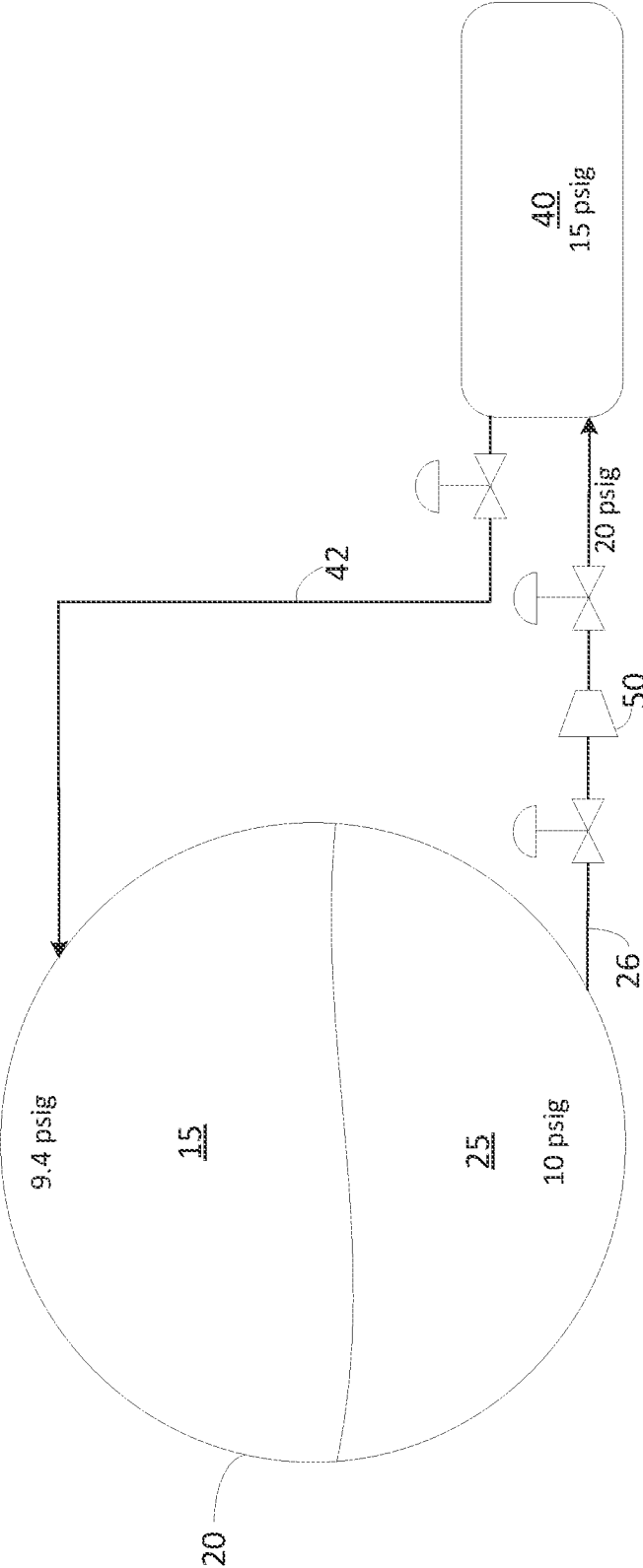
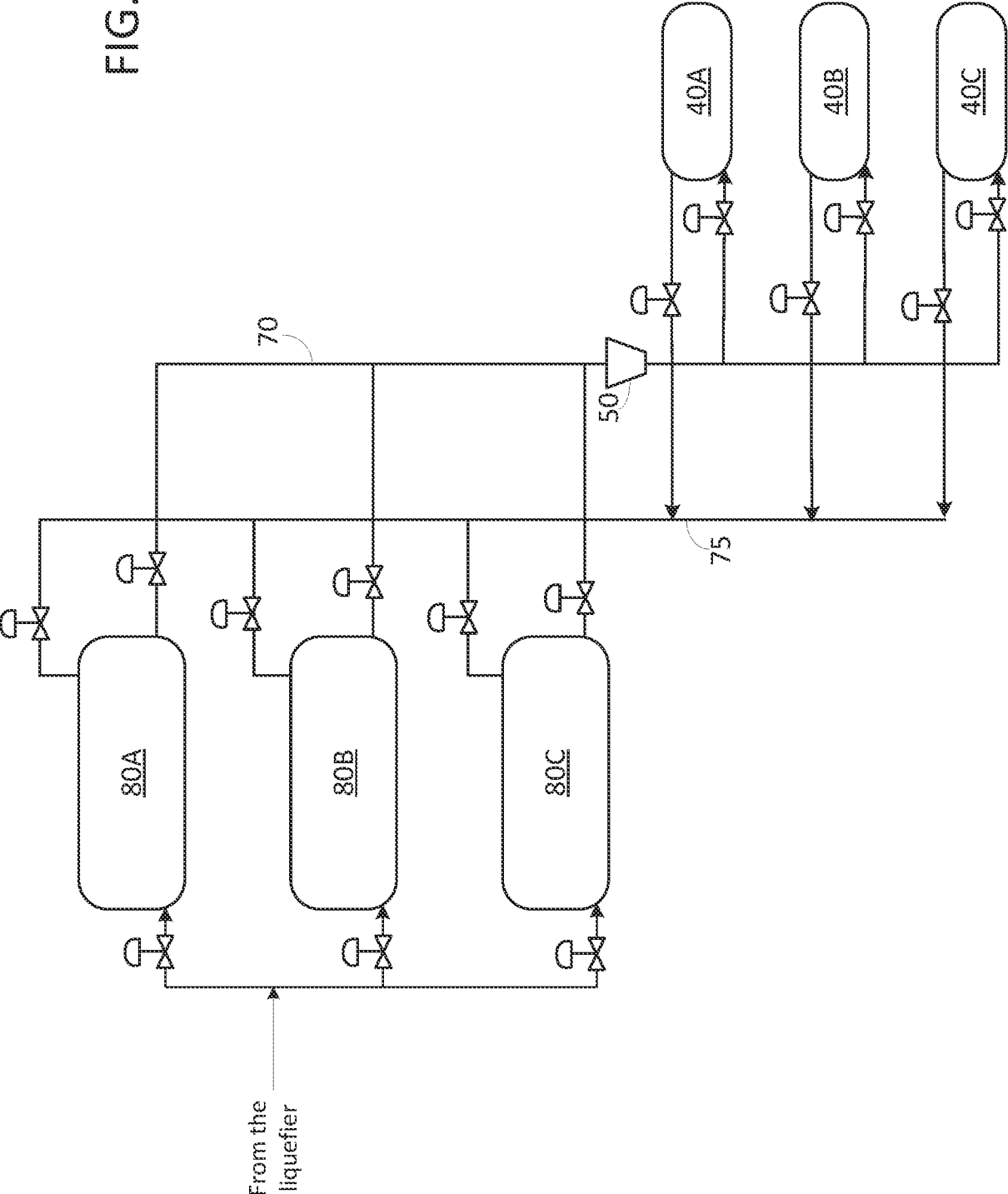


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2024/000390

A. CLASSIFICATION OF SUBJECT MATTER

INV. F17C13/00

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

F17C F25J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

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A	paragraphs [0019] - [0021], [0025]; claims 1-2; figures -----	5 - 14
A	CA 3 238 145 A1 (AZANE FUEL SOLUTIONS AS [NO]) 25 May 2023 (2023-05-25)	5 - 14
	paragraphs [0001], [0015], [0025], [0031]; claim 1; figures -----	
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	claim 1; figures ----- - / - -	



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

20 November 2024

Date of mailing of the international search report

03/12/2024

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2024/000390

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