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(54) **PROCESS FOR PRECOOLING HYDROGEN FOR LIQUEFACTION WITH SUPPLEMENT LIQUID NITROGEN**

(57) A hydrogen feed stream is introduced into a primary refrigeration system of a precooling system and cooling the hydrogen stream to a first precooling temperature. From there, the precooled hydrogen stream is then introduced to a secondary refrigeration system of

the precooling system and cooling the precooled hydrogen stream to a second temperature. Next, the cooled hydrogen stream is then liquefied in the liquefaction system to produce liquid hydrogen.

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Description**CROSS REFERENCE OF RELATED APPLICATIONS**

5 **[0001]** This application claims priority to U.S. Provisional Application Ser. No. 63/295,509 filed on December 30, 2021, U.S. Non-Provisional Application Ser. No. 17/896,953 filed on August 26, 2022, and U.S. Non-Provisional Application Ser. No. 17/896,967 filed on August 26, 2022, all of which are hereby incorporated by reference in their entireties.

TECHNICAL FIELD

10 **[0002]** The present invention generally relates to a method and apparatus for improving the operation of a hydrogen liquefaction unit.

BACKGROUND OF THE INVENTION

15 **[0003]** In the fight against global warming, hydrogen has been identified as a key molecule for producing sustainable energy. For large consumers of hydrogen, it is most economical to produce the hydrogen proximate the consumer, however, for consumers using applications such as fuel cells, it is simply not possible to connect or tie into existing hydrogen gas lines. As such, delivery of hydrogen in liquid form is seen to be the most viable alternative.

20 **[0004]** As is known, liquefied hydrogen requires extremely low temperatures, high pressures, and well-insulated storing materials in order to minimize the losses associated with boil-off gas, not only during transit and storage, but also during transfer between storage tanks. While these steps of the hydrogen market present their own challenges in the supply chain of deliverable hydrogen to the end user market, there are also efficiencies to be gained in the initial liquefaction of the hydrogen itself.

25 **[0005]** Therefore, the efficient liquefaction of hydrogen is of great importance in order for hydrogen to become an economically viable alternative to fossil fuels.

[0006] Hydrogen gas is typically generated from a feed gas such as natural gas or others using steam methane reforming (SMR), partial oxidation (POX), or autothermal reforming (ATR). Some of these processes, such as the POX, often require pressurized gaseous oxygen that is typically supplied by an air separation unit (ASU).

30 **[0007]** With reference to FIG. 1, which represents a hydrogen liquefaction unit (HLU) of the prior art, high pressure hydrogen gas 2 (e.g., 15-70 bara) is purified and dried and sent to a cold box 10 where it is cooled in a precooling heat exchanger 20 to approximately -180°C to -190°C.

35 **[0008]** Refrigeration for this level of cooling is typically provided by nitrogen, either in a closed loop cycle (not shown) or externally provided LIN 52 from a nearby ASU 50. If using a nitrogen cycle, the nitrogen refrigeration cycle may include a single turbine, multiple turbines, a turbine(s) with booster(s) in addition to mechanical refrigeration unit utilizing ammonia or other refrigerant. Additionally, the nitrogen refrigeration cycle typically employs a multistage nitrogen recycle compressor to complete the closed loop.

40 **[0009]** In alternate methods (figure 1), this level of refrigeration (to between -180°C and -190°C) is provided by injecting a stream of liquid nitrogen (LIN) 62 into the exchanger 20 at approximately -190°C. This nitrogen stream vaporizes and is warmed to near ambient temperature as it exchanges cold with the hydrogen stream(s) 2, which are being cooled. The vaporized nitrogen can be extracted and introduced to gas/liquid separator 60, wherein gaseous nitrogen 64 is withdrawn and used to provide additional refrigeration to the heat exchanger 20. This alternative is less thermodynamically efficient due to large quantities of LIN are required to provide refrigeration over the entire temperature range (therefore typically only used for very small plants) and requires liquid nitrogen to be sourced from a separate nitrogen liquefier 50 (e.g., ASU), which would still require a cycle compressor and turbine boosters due to the large refrigeration demand.

45 **[0010]** The cooled gaseous hydrogen 22 is further cooled and liquefied in liquefaction heat exchanger 30 at approximately -252°C by a second refrigeration cycle (not shown). Refrigeration for this level of cooling can be provided by a closed hydrogen (or helium, or helium/neon mixture) refrigeration cycle with multiple turbines and a hydrogen (or helium, or helium/neon mixture) recycle compressor. This hydrogen (or helium, or helium/neon mixture) compression is very difficult and expensive because of the low molecular weight (MW) or more specifically because these molecules are so small. Therefore it is known in the art to cool stream 22 to as cold temperature as possible in order to minimize expensive refrigeration required by hydrogen (or helium, or helium/neon mixture)

50 **[0011]** U.S. Pat. No. 2,983,585 (Smith) discloses a partial oxidation process in which methane is partially oxidized with oxygen to produce carbon monoxide and hydrogen gas. The partial oxidation process is integrated with a hydrogen liquefaction process in which hydrogen gas is pre-cooled by indirect heat exchange against liquid methane and subsequently further cooled against a closed external refrigerating cycle using liquid nitrogen ("LIN") as the refrigerant. The resultant methane is compressed at the warm end of the liquefaction process and then fed to the partial oxidation process. The resultant gaseous nitrogen is compressed at the warm end of the closed cycle before being condensed by

indirect heat exchange with liquid methane and recycled. It is disclosed that the liquid methane could be replaced with liquefied natural gas ("LNG"). However, with this scheme this warm end refrigeration load is simply shifted from the hydrogen liquefier unit to the natural gas liquefaction unit. An additional heat exchange system between nitrogen and LNG is required incurring additional thermodynamic losses. In addition, the hydrogen stream is only cooled to approximately

-150°C due to the liquefaction temperature of LNG.

[0012] U.S. Pat. No. 3,347,055 (Blanchard et al.) discloses a process in which a gaseous hydrocarbon feedstock is reacted to produce hydrogen gas, which is then liquefied in an integrated liquefaction cycle. In one embodiment, the liquefaction cycle involves two closed refrigerant cycles, the first using hydrogen gas as a refrigerant and the second using nitrogen. Compression for both refrigeration cycles takes place at the warm end of the cycles. The hydrogen to be liquefied is also cooled by indirect heat exchange against a liquefied hydrocarbon feedstock gas thereby producing gaseous feedstock at 1 atm. (e.g., about 0.1 MPa) for use in the hydrogen production plant. It is disclosed that the hydrocarbon feedstock may be natural gas. This scheme also is shifting part of the refrigeration load from the hydrogen liquefier to the natural gas liquefier.

[0013] JP-A-2002/243360 discloses a process for producing liquid hydrogen in which hydrogen that is similar to 3,347,055 Blanchard, feed gas is pre-cooled by indirect heat exchange against a stream of pressurized LNG. The pre-cooled hydrogen gas is fed to a liquefier where it is further cooled by indirect heat exchange against both LIN and a refrigerant selected from hydrogen or helium. The further cooled hydrogen is then expanded to produce partially condensed hydrogen, which is separated into liquid hydrogen, which is removed and stored, and hydrogen vapor, which is recycled in the liquefier.

[0014] Quack discloses ("Conceptual Design of a High Efficiency Large Capacity Hydrogen Liquefier"; Adv. Cryog. Eng., Proc. CEC, Madison 2001, AIP, Vol. 613, 255-263) a hydrogen liquefier cycle that, to the inventors knowledge, most accurately represents the best current technology projections for hydrogen liquefaction cycles. It should be noted that Quack uses efficiency figures for compressors and turbines that are not achievable at present, but which are thought to be realistic for the future.

[0015] Current hydrogen liquefaction processes consume power at a rate of about 11 kWh/kg (liquid hydrogen) based on a gaseous hydrogen feed at a typical pressure of 2.5 MPa (25 bar). Quack ("Conceptual Design of a High Efficiency Large Capacity Hydrogen Liquefier"; Adv. Cryog. Eng., Proc. CEC, Madison 2001, AIP, Vol. 613, 255-263) suggests that the best future power consumption will be in the range 5 to 7 kWh/kg (liquid hydrogen) if his suggested improvements are utilized.

[0016] This scheme involves pre-cooling the hydrogen to about -53°C by indirect heat exchange with propane, ammonia, fluorocarbons or other refrigerants. The hydrogen is then further cooled and liquefied in two or more steps by indirect heat exchange against a mixture of helium and neon. The use of neon increases the molecular weight of the refrigerant mixture making it easier for the recycle compressor and thereby reducing compression energy (generally 75% He of MW=4 and 25% Ne of MW=20 having a mixture of MW=8). However, the use of neon in the mixture also prevents the temperature level of the refrigerant from achieving the very cold temperatures (-252°C) required for the liquefaction of hydrogen. In addition, helium and neon must be sourced and its composition in the neon/helium mixture carefully managed. In addition, this refrigerant must be compressed specifically and solely for the purpose of the hydrogen liquefaction energy.

[0017] It is an object of the present invention to develop a scheme, which provides a process and apparatus for improving the efficiencies of the hydrogen liquefaction unit, particularly the precooling of hydrogen to between -180C and -190C.

BRIEF SUMMARY OF THE INVENTION

[0018] The present invention is directed to a device and a method that satisfies at least one of these needs. One objective of the current invention is to improve the refrigeration section for the precooling portion (e.g., 300K to about 80K) of the hydrogen liquefaction process, while also minimizing the number of rotating equipment (e.g., compressors and turbine boosters). In certain embodiments, the invention can include integration of an air separation unit (ASU), a hydrogen generation unit (HGU), and a hydrogen liquefaction unit (HLU), wherein the ASU provides pressurized gaseous oxygen to the HGU, and the HGU provides gaseous hydrogen to the HLU. The HLU includes a precooling unit having a primary refrigeration system and a secondary refrigeration system, and a liquefaction system. The precooling unit is configured to cool the hydrogen to approximately 80K, while the liquefaction unit is configured to cool and liquefy the hydrogen to a temperature suitable for liquefaction of the hydrogen as is known in the art.

[0019] In an additional embodiment, the ASU can provide liquid nitrogen to the HLU, preferably for use as the refrigerant for the secondary refrigeration system of the precooling step. This nitrogen for the secondary refrigeration system is preferably never combined or mixed with the primary refrigeration system.

[0020] In certain embodiments, the integrated system of ASU, HLU, and HGU includes a single air compressor while providing refrigeration to the HLU at the ~80K level with a single nitrogen cycle compressor (e.g., no low-pressure feed/flash gas nitrogen compressor). In another embodiment, it is preferred to provide liquid nitrogen (LIN) for vaporization within the precooling unit of the HLU, such that the vaporized LIN is not directly combined with the primary precooling cycle

(N₂ turbo expander cycle).

[0021] In one embodiment, a method for liquefaction of hydrogen in a hydrogen liquefaction unit is provided. The method can include the steps of: introducing a hydrogen stream into a precooling system under conditions effective for cooling the hydrogen stream to a temperature of between about 75K and about 100K, more preferably between about 80K and about 90K, more preferably of about 80K to produce a cooled hydrogen stream, wherein the precooling system comprises a primary refrigeration system and a secondary refrigeration system; introducing the cooled hydrogen stream to a liquefaction system under conditions effective for liquefying the cooled hydrogen stream to produce liquid hydrogen; and withdrawing the liquid hydrogen from the liquefaction system.

[0022] In optional embodiments of the method for liquefaction of hydrogen in a hydrogen liquefaction unit:

- the hydrogen stream is sourced from a hydrogen generation unit;
- the primary refrigeration system is configured to provide cooling within the precooling system to a first temperature between about 100K and about 120K;
- the first temperature is within about 30K of a vaporization temperature of liquid nitrogen used within the secondary refrigeration system;
- the primary refrigeration system uses refrigeration produced by a refrigerant selected from the group consisting of mixed hydrocarbon refrigerant, nitrogen, argon, fluorocarbon as part of a closed loop refrigeration cycle, vaporization of liquid nitrogen, ammonia, and combinations thereof;
- the secondary refrigeration system is configured to provide cooling within the precooling system to a temperature of between about 75K and about 100K, more preferably of about 80K;
- the secondary refrigeration system comprises vaporization of liquid nitrogen, wherein the liquid nitrogen is received from an air separation unit;
- the vaporization of liquid nitrogen in the secondary refrigeration system occurs at a vaporization pressure that is less than a discharge pressure of a cold turbine used within the primary refrigeration system;
- the method can also include the step of providing an air separation unit and a hydrogen generation unit, wherein the air separation unit is configured to produce an oxygen stream and a liquid nitrogen stream, wherein the air separation unit is in fluid communication with the hydrogen generation unit and the secondary refrigeration system, such that the air separation is configured to send the oxygen stream to the hydrogen generation unit and the liquid nitrogen to the secondary refrigeration system;
- the liquid nitrogen has a flow rate of 0 to 50% of a flow rate of the oxygen stream sent to the hydrogen generation unit;
- the method can also include the step of recycling a vaporized nitrogen stream from the hydrogen liquefaction unit to the air separation unit; and/or
- the air separation unit comprises a high pressure feed air compressor;
- the air separation unit is a GOK type air separation unit; and/or
- the air separation unit can include a high pressure (>15 bara) main air compressor (i.e., GOK type) air separation unit.

[0023] In another embodiment, a method for liquefaction of hydrogen in a hydrogen liquefaction unit is provided. The method can include the steps of: introducing a hydrogen stream into a precooling system under conditions effective for cooling the hydrogen stream to a temperature of between about 75K and about 100K, more preferably between about 80K and about 90K, more preferably of about 80K to produce a cooled hydrogen stream, wherein the precooling system comprises a primary refrigeration system and a secondary refrigeration system; introducing the cooled hydrogen stream to a liquefaction system under conditions effective for liquefying the cooled hydrogen stream to produce liquid hydrogen; and withdrawing the liquid hydrogen from the liquefaction system; wherein the primary refrigeration system comprises compression and expansion of a primary refrigerant with expansion outlet pressure of P_1 and a secondary refrigeration system comprises vaporization of liquid nitrogen at pressure P_2 ; wherein the primary and secondary refrigerants are not in fluid communication.

[0024] In optional embodiments of the method for liquefaction of hydrogen in a hydrogen liquefaction unit:

- P_1 is at least 0.5 bar greater than P_2 ;
- the method can also include the step of providing an air separation unit and a hydrogen generation unit, wherein the air separation unit is configured to produce an oxygen stream and a liquid nitrogen stream, wherein the air separation unit is in fluid communication with the hydrogen generation unit and the secondary refrigeration system, such that the air separation unit is configured to send the oxygen stream to the hydrogen generation unit and the liquid nitrogen to the secondary refrigeration system; and/or
- the liquid nitrogen has a flow rate of about 5% to about 50% of a flow rate of the oxygen stream sent to the hydrogen generation unit.

[0025] In another embodiment, an integrated industrial unit is provided, which can include: a nitrogen source configured

to provide liquid nitrogen; a hydrogen source configured to provide gaseous hydrogen at a pressure of at least 15 bar(a); a hydrogen liquefaction unit, wherein the hydrogen liquefaction unit comprises a precooling system, and a liquefaction system; and a liquid hydrogen storage tank, wherein the precooling system is configured to receive the gaseous hydrogen from the hydrogen source and cool the gaseous hydrogen to a temperature between 75K and 100K, wherein the precooling system comprises a primary refrigeration system and a secondary refrigeration system, wherein the liquefaction system is in fluid communication with the precooling system and is configured to liquefy the gaseous hydrogen received from the precooling system to produce liquid hydrogen, wherein the liquid hydrogen storage tank is in fluid communication with the liquefaction system and is configured to store the liquid hydrogen received from the liquefaction system.

[0026] In optional embodiments of the integrated industrial unit:

- the hydrogen source is a hydrogen generation unit, and the nitrogen source is an air separation unit;
- the air separation unit is configured to produce an oxygen stream and a liquid nitrogen stream, wherein the air separation unit is in fluid communication with the hydrogen generation unit and the secondary refrigeration system, such that the air separation unit is configured to send the oxygen stream to the hydrogen generation unit and the liquid nitrogen to the secondary refrigeration system;
- the integrated industrial unit can include a flow controller configured to control a flow rate of the liquid nitrogen such that the flow rate of the liquid nitrogen from the nitrogen source is between 5 to 50% of a flow rate of the oxygen stream sent to the hydrogen generation unit;
- the air separation unit is configured to receive a recycled a vaporized nitrogen stream from the hydrogen liquefaction unit;
- the air separation unit comprises a high pressure feed air compressor;
- the primary refrigeration system is configured to provide cooling within the precooling system to a first temperature between about 100K and about 120K;
- the first temperature is within about 30K of a vaporization temperature of liquid nitrogen used within the secondary refrigeration system;
- the first temperature is within about 20K of a vaporization temperature of liquid nitrogen used within the secondary refrigeration system;
- the primary refrigeration system uses refrigeration produced by a refrigerant selected from the group consisting of a hydrocarbon refrigerant, a mixed hydrocarbon refrigerant, nitrogen as part of a closed loop refrigeration cycle, argon, fluorocarbons, vaporization of liquid nitrogen, ammonia, and combinations thereof;
- the secondary refrigeration system is configured to provide cooling within the precooling system to a temperature between about 75K and about 100K, more preferably between about 80K and about 90K;
- the secondary refrigeration system comprises vaporization of liquid nitrogen, wherein the liquid nitrogen is received from an air separation unit; and/or
- the vaporization of liquid nitrogen in the secondary refrigeration system occurs at a vaporization pressure that is less than a discharge pressure of a cold turbine used within the primary refrigeration system.

[0027] In another embodiment, an integrated industrial unit is provided, which can include: a nitrogen source configured to provide liquid nitrogen; a hydrogen source configured to provide gaseous hydrogen at a pressure of at least 15 bar(a); a hydrogen liquefaction unit, wherein the hydrogen liquefaction unit comprises a precooling system, and a liquefaction system; and a liquid hydrogen storage tank, wherein the precooling system is configured to receive the gaseous hydrogen from the hydrogen source and cool the gaseous hydrogen to a temperature between 75K and 100K, wherein the precooling system comprises a primary refrigeration system and a secondary refrigeration system, wherein the liquefaction system is in fluid communication with the precooling system and is configured to liquefy the gaseous hydrogen received from the precooling system to produce liquid hydrogen, wherein the liquid hydrogen storage tank is in fluid communication with the liquefaction system and is configured to store the liquid hydrogen received from the liquefaction system, wherein the primary refrigeration system comprises compressors and expanders configured to compress and expand, respectively, a primary refrigerant, wherein the expanders are configured to have an outlet pressure of P_1 , wherein the secondary refrigeration system provides refrigeration to the precooling system by vaporization of liquid nitrogen at pressure P_2 , wherein the primary and secondary refrigerants are not in fluid communication.

[0028] In optional embodiments of the integrated industrial unit:

- P_1 is at least 0.5 bar greater than P_2 ;
- the hydrogen source is a hydrogen generation unit, and the nitrogen source is an air separation unit;
- the air separation unit is configured to produce an oxygen stream and a liquid nitrogen stream, wherein the air separation unit is in fluid communication with the hydrogen generation unit and the secondary refrigeration system, such that the air separation unit is configured to send the oxygen stream to the hydrogen generation unit and the liquid

nitrogen to the secondary refrigeration system;

- the integrated industrial unit can include a flow controller configured to control a flow rate of the liquid nitrogen such that the flow rate of the liquid nitrogen from the nitrogen source is between 5 to 50% of a flow rate of the oxygen stream sent to the hydrogen generation unit;
- the air separation unit comprises a high pressure feed air compressor;
- the primary refrigeration system is configured to provide cooling within the precooling system to a first temperature between about 100K and about 120K;
- the first temperature is within about 20K of a vaporization temperature of liquid nitrogen used within the secondary refrigeration system;
- the primary refrigeration system uses refrigeration produced by a refrigerant selected from the group consisting of a hydrocarbon refrigerant, a mixed hydrocarbon refrigerant, nitrogen as part of a closed loop refrigeration cycle, argon, fluorocarbons, vaporization of liquid nitrogen, ammonia, and combinations thereof;
- the secondary refrigeration system is configured to provide cooling within the precooling system to a temperature of about 80K to about 90K;
- the secondary refrigeration system comprises vaporization of liquid nitrogen, wherein the liquid nitrogen is received from an air separation unit; and/or
- the vaporization of liquid nitrogen in the secondary refrigeration system occurs at a vaporization pressure that is less than a discharge pressure of a cold turbine used within the primary refrigeration system

[0029] The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter, which form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiment disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims. The novel features, which are believed to be characteristic of the invention, both as to its organization and method of operation, together with further objects and advantages, will be better understood from the following description when considered in connection with the accompanying figures. It is to be expressly understood, however, that each of the figures is provided for the purpose of illustration and description only and is not intended as a definition of the limits of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a process flow diagram of an embodiment of the prior art.

FIG. 2 is flow chart in accordance with an embodiment of the present invention.

FIG 3. is a schematic diagram of an embodiment of the present invention.

FIG 4. is a schematic diagram of an Air Separation Unit in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0031] 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.

[0032] Certain embodiments of the invention can include integration of an air separation unit (ASU), a hydrogen generation unit (HGU), and a hydrogen liquefaction unit (HLU), wherein the ASU provides pressurized gaseous oxygen to the HGU, and the HGU provides gaseous hydrogen to the HLU. The HLU includes a precooling unit having a primary refrigeration system and a secondary refrigeration system, and a liquefaction system. The precooling unit is configured to cool the hydrogen to approximately 80K, while the liquefaction unit is configured to cool and liquefy the hydrogen.

[0033] FIG. 2 provides a flow chart in accordance with an embodiment of the present invention. A hydrogen feed stream 2 is introduced into a primary refrigeration system of a precooling system and cooling the hydrogen stream to a first precooling temperature. From there, the precooled hydrogen stream is then introduced to a secondary refrigeration system of the precooling system and cooling the precooled hydrogen stream to a second temperature. Next, the cooled hydrogen stream 22 is then liquefied in the liquefaction system to produce liquid hydrogen 32.

Air Separation Unit

[0034] In order to avoid expensive external gaseous oxygen compression, oxygen is typically compressed by pumping liquid oxygen (LOX) and vaporizing it at high pressure in a main heat exchanger by heat exchange with another condensing stream (typically air). The condensing stream may either be at a higher pressure than the oxygen (for example using an additional BAC (booster air compressor)), or lower pressure than the oxygen (for example without a BAC using higher pressure from the MAC, a.k.a. GOK - See, e.g., U.S. Pat. 5,329,776].

[0035] A significant advantage of this "GOK" cycle is the ability to produce pressurized gaseous oxygen with a single air compressor (without the BAC). With this process, the pressure from the MAC must be sufficient to meet the cold end refrigeration requirements to vaporize the oxygen. However, it also yields excessive refrigeration at the mid and warm ends, which are often valorized by either a) producing LOX, LIN and/or LAR (i.e., fatal liquid) or b) adding a cold booster, which adds heat to the process. See, e.g., U.S. Pat. 5,475,980.

[0036] It is therefore desirable to find a process which can valorize this available "fatal liquid" (free refrigeration) from an ASU with a single MAC.

[0037] Similarly, for other ASU process cycles, refrigeration to produce incremental LIN can be available at very low cost relative to other operations such as the precooling portion of a hydrogen liquefier. In one example, the specific power of incremental LIN is only 0.3kW/Nm³ from the ASU but 0.6kW/Nm³ in the HLU.

Hydrogen Liquefaction Unit

[0038] Hydrogen liquefaction processes require refrigeration over a very wide temperature range (300K to 20K). It is common to have separate dedicated refrigeration systems for the warm end (300K to 80K) and the cold end (80K to 20K) since the specific refrigeration demands and cost vary significantly with temperature. Regarding the warm temperature range (300K to 80K): existing technology uses a) closed loop N₂ cycle, b) vaporization of LIN from an ASU, or c) mixed hydrocarbon refrigerant.

[0039] Mixed hydrocarbon refrigerant can be the most thermodynamically efficient; however, it can also be the most expensive and is limited to process cooling to 95K to 100K before freezing hydrocarbon components and/or multi liquid phase problems. Therefore, an additional refrigeration load must be added to cover the range between 80K and 100K. This range is often compensated by additional load on the very cold refrigeration system (i.e. H₂ or He) but at a prohibitive cost. Therefore, it is desirable to have another means for this range of refrigeration.

[0040] Additionally, for small liquefiers where OPEX is less important, refrigeration for the full temperature range of 300K to 80K can be achieved by providing LIN from either local ASU or merchant, and vaporizing in the main exchanger. Although LIN can provide efficient refrigeration in the temperature range somewhat above 80K, it is not thermodynamically efficient for LIN to provide this complete temperature range up to 300K. As a result, this is typically limited to small liquefiers due to the extremely large quantities of LIN required making this unfeasible for large liquefiers.

[0041] In embodiments that use a nitrogen refrigeration cycle, the N₂ refrigeration cycle involves compression of N₂, partial cooling and expansion in dual turbine boosters. A portion of the high pressure N₂ is further cooled and expanded to 1.2 to 2 bara with a JT valve forming LIN, which is then vaporized providing refrigeration to the cooling streams at ~80K. It is desirable for this LIN vaporization pressure to be as low as possible (e.g., 1.2 bar(a)) to provide the coldest temperature level, which is typically limited by pressure drop to rewarm and feed a low-pressure flash gas compressor. However, it is desirable to have a solution with a single recycle compressor without the additional feed/flash gas compressor.

[0042] In a preferred embodiment, the ASU can use a single MAC scheme in accordance with the GOK ASU process as described above. This provides high-pressure oxygen (e.g., 30-40 bar(a)) to the HGU and liquid nitrogen (LIN) in a flow range of 15-50% of oxygen separation to the HLU, more preferably 25-40%. LAR can also optionally be produced.

[0043] In a preferred embodiment, at least a portion of the LIN provides refrigeration to supplement the primary precooling refrigeration of the HLU. Where the primary precooling refrigeration may include a nitrogen turbo expander cycle, mixed hydrocarbon refrigerant cycle, ammonia cycle or similar.

[0044] In certain embodiments, the LIN sent to the HLU is used for refrigeration purposes only, and therefore, high purity nitrogen is not required. For example, purities of <1% O₂ as limited by margin to lower explosive limit of H₂ is sufficient.

[0045] In certain embodiments, the quantity of GOX from the ASU to the HGU can be proportional to the quantity of H₂ produced and liquefied. The quantity of LIN to be vaporized in the HLU can be a function of the quantity of H₂ to be liquefied as well as the range of temperatures to which it is to provide cooling in the HLU. This temperature range in the HLU is from points 1 and 2 where Point 1 is the vaporization temperature of LIN at the lowest feasible pressure (dP of main exchanger only since it can be vented rather than feed an LP compressor). Point 2: the minimum temperature of the primary precooling refrigeration system. For N₂ turbo-expansion cycle, point 2 is the discharge temperature of the cold turbine. For mixed HC refrigerant cycle, point 2 is the minimum temperature of the HC mixed refrigerant.

[0046] In certain embodiments, the quantity of LIN to be vaporized can increase as the temperature difference between points 1 and 2 increases. If the discharge pressure of the cold N₂ turboexpander (also referred to as a turbo booster)

increases, then its temperature must also increase to prevent liquid formation at the turbine outlet resulting in additional LIN flow to be vaporized.

[0047] There is potential for OPEX savings in addition to the CAPEX savings of compressors, turboexpander equipment and heat exchange area. The optimization is based on the balance of the specific power for LIN produced by the ASU vs LIN produced by the HLU preliminary precooling system in balance with the capex savings indicated above.

[0048] In a preferred embodiment, LIN in the flow range of 15 to 50% of O₂ separation, more preferably 25% to 40% of O₂ separation to the HGU provides an optimum to de-couple the vaporized LIN from the N₂ refrigeration cycle, increasing the pressure of the turbine discharge, thus improving the process.

[0049] As indicated in Table 1 below, the mass quantity of HPGOX needed in the HGU is approximately 3.3x the mass of H₂ produced from the HGU and to be liquefied in the HLU. As indicated earlier, the GOK-type ASU (typically with single high pressure MAC) is a low equipment cost ASU that produces "fatal" liquid refrigeration at very low energy cost. This ASU scheme is well suited for producing LIN in the range of about 25% to 40% of the O₂ separation mass flow. The temperature difference (between cold end of primary refrigerant and vaporizing LIN second refrigerant) is meaningful because it directly determines the quantity of secondary refrigerant LIN needed. By keeping this dT <30K we keep LIN from ASU to HLU in the range of about 25% to 40% of the O₂ separation mass flow for optimal ASU and HLU design.

Table 1

	LIN only (Fig 1)	Proposed (Fig 3)
LH2	55mtd	55mtd
HPGOX to HGU	183mtd	183mtd
LIN to HLU	501 mtd	65mtd
LIN as % of GOX	273%	36%
Power to produce LIN	9168kW (at0.55kW/Nm3)	758kW (at0.35kW/Nm3)
N2 cycle (primary refig)	0 kW	5094kW
Net Precooling power	9168kW	5852kW (62% less)

[0050] FIG. 2 provides a schematic process view of an embodiment of the present invention in which an HLU 10 is integrated with both an HGU 40 and an ASU 50. In the embodiment shown, an air feed 4 is introduced into ASU 50 in order to produce liquid nitrogen 52 and gaseous oxygen 54. Gaseous oxygen 54 is then introduced into HGU 40, which can be an SMR, ATR, POX or the like, wherein a feed stream (not shown) is used along with gaseous oxygen 54 to produce high-pressure hydrogen 2.

[0051] HLU 10 preferably comprises a precooling system 20, a liquefying system 30, a primary refrigeration system 70, a secondary refrigeration system (62,64), and a thermal insulator such as a cold-box (not shown), which provides thermal insulation for certain equipment within HLU 10 that will be exposed to temperatures below freezing. Precooling system 20 and liquefying system 30 preferably include heat exchangers configured to operate at cryogenic temperatures and exchange heat between two or more stream via indirect heat exchange. The types of heat exchangers used in certain embodiments can be chosen appropriately by one of ordinary skill in the art.

[0052] High-pressure hydrogen 2 is then introduced to HLU 10, wherein it is first cooled in precooling section 20 to a temperature of about 80K to form cooled hydrogen stream 22. This stream 22 is then sent to liquefying system 30 under conditions effective for liquefying the cooled hydrogen stream 22 to produce liquid hydrogen 32, which is withdrawn as a product stream.

[0053] Refrigeration for this level of cooling can be provided by a closed hydrogen (or helium) refrigeration cycle with multiple turbines and a hydrogen (or helium) recycle compressor. This hydrogen (or helium) compression is very difficult and expensive because of the low molecular weight (MW) or more specifically because these molecules are so small.

[0054] Those of ordinary skill in the art will also recognize that production of liquid hydrogen requires other steps (e.g., adsorption systems, ortho - para conversion) which are not described herein as they are not impacted by embodiments of the current invention.

[0055] Refrigeration needed to provide the cooling to produce cooled hydrogen stream 22 is provided by primary refrigeration system 70 and secondary refrigeration system 62/64. In the embodiment shown, primary refrigeration system is a closed loop nitrogen refrigeration cycle comprising a recycle compressor 75, and first and second turbo boosters 85, 95. As the boosters of the turbo boosters are powered by turbines, the only power used in this refrigeration cycle is from the recycle compressor 75.

[0056] In the embodiment shown, secondary refrigeration system comprises vaporizing LIN 52 received from ASU 50. In this embodiment, LIN 52 is introduced to gas/liquid separator 60 wherein the liquid nitrogen 62 is withdrawn from a bottom

portion of gas/liquid separator 60 and warmed in precooling section 20, wherein it is then withdrawn and sent back to gas/liquid separator 60. Gaseous nitrogen 64 is withdrawn from a top portion of gas/liquid separator 60 before being sent to precooling section 20 for warming therein. Gaseous nitrogen is withdrawn from the warm end of the precooling section 20 and either captured for further use or vented to the atmosphere.

[0057] FIG. 3 provides a detailed view of an embodiment using a GOK-type ASU in accordance with an embodiment of the present invention, in which the ASU also includes a turbo booster 170, 180. Referring to FIG. 3, first air stream 102 is compressed in first MAC 110 to form compressed stream 112, before being fed to front-end purification unit (FEP) 130 to remove components that might freeze at cryogenic temperatures (e.g., water and carbon dioxide). The MAC preferably pressurizes stream 112 to an appropriate pressure level as is known by those of ordinary skill in the art, such that first portion 134 can be appropriately separated in the distillation column system 150.

[0058] In the embodiment shown that includes turbo booster 170, 180, purified air stream 132 is split into a first portion 134 and a second portion 136. First portion 134 is kept at substantially the same pressure as the discharge of the MAC (minus pressure losses inherent in piping and equipment) and then introduced into a warm end of the main heat exchanger 140. After cooling in main heat exchanger 140, cooled first stream 142 is then introduced into distillation column system 150 for separation therein.

[0059] Second portion 136 is further compressed in warm booster 170 to form boosted stream 172. The embodiment shown preferably includes cooler 171 in order to remove heat of compression from boosted stream 172 prior to introduction to main heat exchanger 140. In the embodiment shown, warm booster 170 is coupled to turbine 180; thereby forming what is commonly referred to as a turbo-booster, which allows for the spinning of the turbine 180 to power the warm booster 170.

[0060] Boosted stream 172 can then be sent to main heat exchanger 140 for cooling, wherein first portion 174 is withdrawn at an intermediate location and then expanded in turbine 180 to form expanded air 182, which is then introduced to distillation column system 150 for separation therein. Second portion 144 is fully cooled in heat exchanger 140 and then expanded across a Joule-Thompson valve 145 to produce additional refrigeration for the system before being introduced to the distillation column system for separation therein.

[0061] In the embodiment shown, distillation column system 150 is configured to provide a waste nitrogen stream 151, a medium pressure nitrogen stream 153, a low-pressure nitrogen stream 155 and a high-pressure gaseous oxygen stream 54. In the embodiment shown, liquid oxygen 152 is withdrawn from the sump of the lower-pressure column (not shown) and pressurized in pump 200 before being heated in main heat exchanger 140 to form high-pressure gaseous oxygen stream 54. Liquid nitrogen product 52 can also be withdrawn from the distillation column system.

[0062] Embodiments of the current invention provide improved means of operation, particularly with respect to operation of turbines. For example, in methods known heretofore, turndown is limited because turbine outlet pressure is fixed and equal to LIN vapor pressure. Turndown of the refrigeration loop can only be with flow and is limited by the machines to ~70%-80% of design (for example approach to compressor surge,...). However, in certain embodiments of the present invention, the primary refrigerant (e.g., N₂ expansion or mixed refrigerant) is independent of the secondary refrigerant (LIN vaporization). The pressures throughout the primary refrigerant loop may be significantly reduced such that pressure ratios across all machines can be maintained approximately constant and operating near their best efficiency points. In certain embodiments, this yields efficient turndown to approximately <30% of design.

[0063] As used herein, "turndown" is meant to include an operating case with reduced LH₂ production flowrates. In order to achieve this, the precooling refrigeration system and cold end refrigeration system would also both need the ability to reduce refrigeration correspondingly. However, the methods known heretofore do not have much capability beyond operating at about 70-80% of design, whereas embodiments of the present invention have the capability to operate at less than 30% of design. This provides a distinct advantage in cases where demand lowers for whatever reason.

[0064] Those of ordinary skill in the art will recognize that the distillation column system 150 can be any column system that is configured to separate air into at least a nitrogen-enriched stream and an oxygen-enriched stream. This can include a single nitrogen column or a double column having a higher and lower pressure column, as is known in the art. In another embodiment, the distillation column system can also include other columns such as argon, xenon, and krypton columns. As all of these columns and systems are well known in the art, Applicant is not including detailed figures pertaining to their exact setup, as they are not necessary for an understanding of the inventive aspect of the present invention.

[0065] As used herein, a high pressure feed air compressor can include an air compressor with an output pressure of at least 15 bar(a). Additionally, as used herein, the term "about" can include natural variations that occur and include a generally accepted error range. In certain embodiments, about can include +/- 5% of a particular value.

[0066] Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the invention as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the disclosure of the present invention, processes, machines, manufacture, compositions of matter, means, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the

corresponding embodiments described herein may be utilized according to the present invention. Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

[0067] 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 or reversed in order.

[0068] The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

[0069] "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.

[0070] "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 a range is expressed, it is to be understood that another embodiment is from the one.

[0071] 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.

[0072] Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such particular value and/or to the other particular value, along with all combinations within said range.

[0073] All references identified herein are each hereby incorporated by reference into this application in their entireties, as well as for the specific information for which each is cited.

Claims

1. A method for liquefaction of hydrogen in a hydrogen liquefaction unit, the method comprising the steps of:

introducing a hydrogen stream into a precooling system under conditions effective for cooling the hydrogen stream to a temperature of between about 75K and about 100K, , more preferably between about 80K and about 90K, more preferably of about 80K, to produce a cooled hydrogen stream, wherein the precooling system comprises a primary refrigeration system and a secondary refrigeration system;

introducing the cooled hydrogen stream to a liquefaction system under conditions effective for liquefying the cooled hydrogen stream to produce liquid hydrogen; and withdrawing the liquid hydrogen from the liquefaction system;

wherein the primary refrigeration system comprises compression and expansion of a primary refrigerant with expansion outlet pressure of P_1 and a secondary refrigeration system comprises vaporization of liquid nitrogen at pressure P_2 ;

wherein the primary and secondary refrigerants are not in fluid communication;

wherein P_1 is at least 0.5 bar greater than P_2 .

2. The method as claimed in claim 1, further comprising the step of providing an air separation unit and a hydrogen generation unit, wherein the air separation unit is configured to produce an oxygen stream and a liquid nitrogen stream, wherein the air separation unit is in fluid communication with the hydrogen generation unit and the secondary refrigeration system, such that the air separation unit is configured to send the oxygen stream to the hydrogen generation unit and the liquid nitrogen to the secondary refrigeration system.

3. The method as claimed in claim 2, wherein the liquid nitrogen has a flow rate of about 5% to about 50% of a flow rate of the oxygen stream sent to the hydrogen generation unit.

4. An integrated industrial unit comprising:

a nitrogen source configured to provide liquid nitrogen;

a hydrogen source configured to provide gaseous hydrogen at a pressure of at least 15 bar(a);

a hydrogen liquefaction unit, wherein the hydrogen liquefaction unit comprises a precooling system, and a liquefaction system; and

a liquid hydrogen storage tank,

wherein the precooling system is configured to receive the gaseous hydrogen from the hydrogen source and cool the gaseous hydrogen to a temperature between 75K and 100K,

wherein the precooling system comprises a primary refrigeration system and a secondary refrigeration system, wherein the liquefaction system is in fluid communication with the precooling system and is configured to liquefy the gaseous hydrogen received from the precooling system to produce liquid hydrogen, wherein the liquid hydrogen storage tank is in fluid communication with the liquefaction system and is configured to store the liquid hydrogen received from the liquefaction system, wherein the primary refrigeration system comprises compressors and expanders configured to compress and expand, respectively, a primary refrigerant, wherein the expanders are configured to have an outlet pressure of P_1 , wherein the secondary refrigeration system provides refrigeration to the precooling system by vaporization of liquid nitrogen at pressure P_2 , wherein the primary and secondary refrigerants are not in fluid communication; wherein P_1 is at least 0.5 bar greater than P_2 .

5. The integrated industrial unit as claimed in claim 4, wherein the hydrogen source is a hydrogen generation unit, and the nitrogen source is an air separation unit, wherein the air separation unit is configured to produce an oxygen stream and a liquid nitrogen stream, wherein the air separation unit is in fluid communication with the hydrogen generation unit and the secondary refrigeration system, such that the air separation unit is configured to send the oxygen stream to the hydrogen generation unit and the liquid nitrogen to the secondary refrigeration system.
6. The integrated industrial unit as claimed in claim 5, further comprising a flow controller configured to control a flow rate of the liquid nitrogen such that the flow rate of the liquid nitrogen from the nitrogen source is between 5 to 50% of a flow rate of the oxygen stream sent to the hydrogen generation unit.
7. The integrated industrial unit as claimed in claim 5, wherein the air separation unit comprises a high pressure feed air compressor.
8. The integrated industrial unit as claimed in claim 4, wherein the primary refrigeration system is configured to provide cooling within the precooling system to a first temperature between about 100K and about 120K.
9. The integrated industrial unit as claimed in claim 8, wherein the first temperature is within about 20K of a vaporization temperature of liquid nitrogen used within the secondary refrigeration system.
10. The integrated industrial unit as claimed in claim 4, wherein the primary refrigeration system uses refrigeration produced by a refrigerant selected from the group consisting of a hydrocarbon refrigerant, a mixed hydrocarbon refrigerant, nitrogen as part of a closed loop refrigeration cycle, argon, fluorocarbons, vaporization of liquid nitrogen, ammonia, and combinations thereof.
11. The integrated industrial unit as claimed in claim 4, wherein the secondary refrigeration system is configured to provide cooling within the precooling system to a temperature of about 80K to about 90K.
12. The integrated industrial unit as claimed in claim 4, wherein the secondary refrigeration system comprises vaporization of liquid nitrogen, wherein the liquid nitrogen is received from an air separation unit.
13. The integrated industrial unit as claimed in claim 12, wherein the vaporization of liquid nitrogen in the secondary refrigeration system occurs at a vaporization pressure that is less than a discharge pressure of a cold turbine used within the primary refrigeration system.

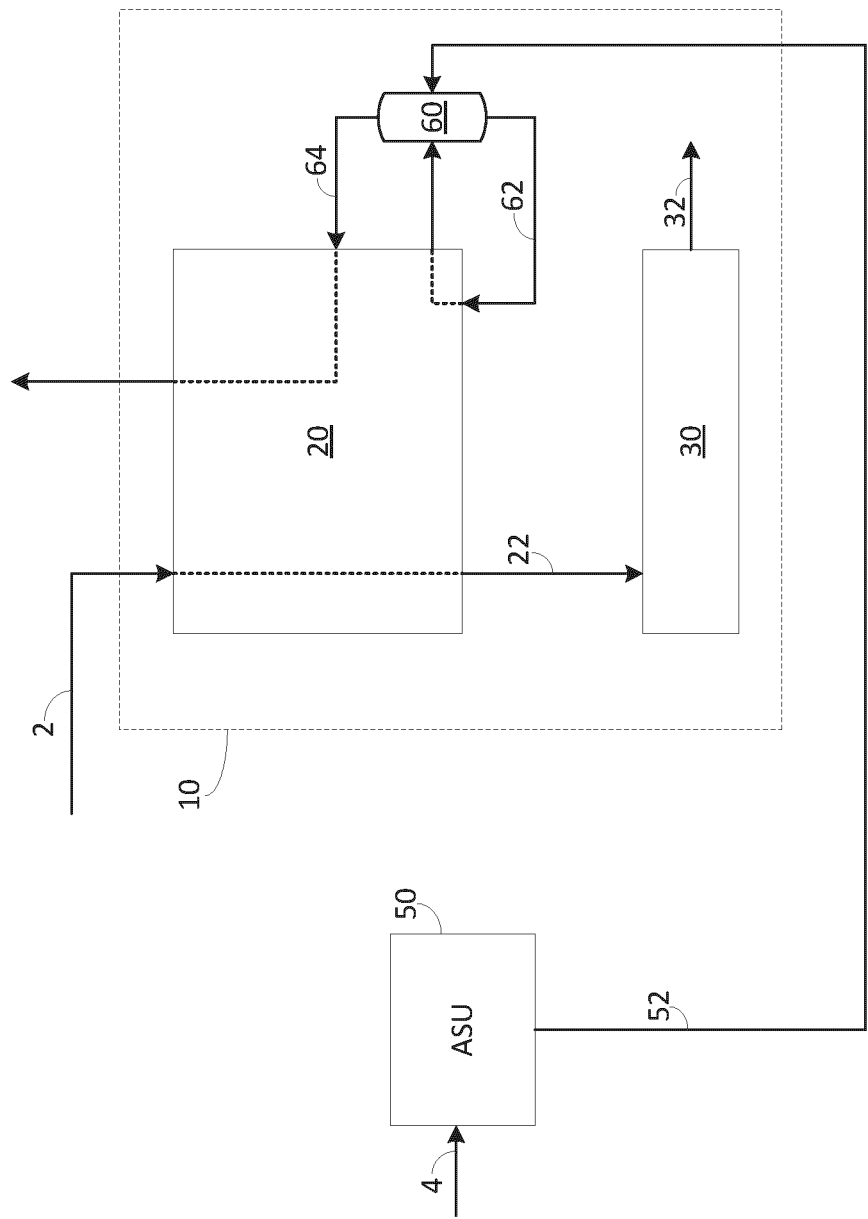


FIG. 1
(Prior Art)

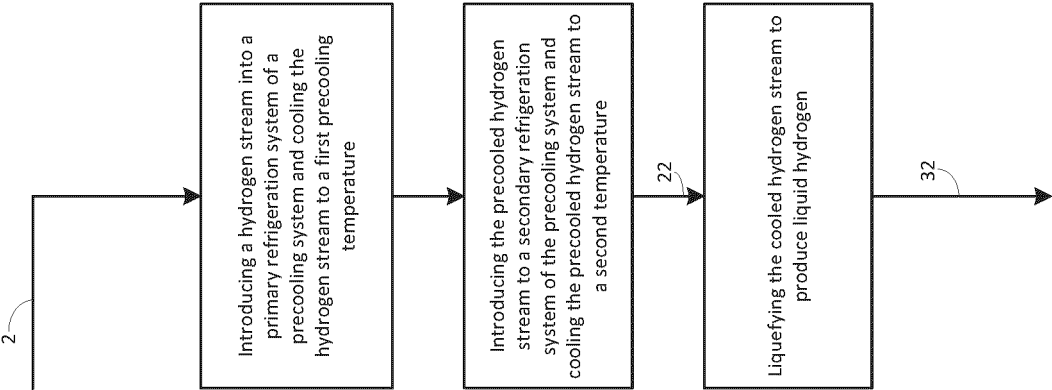


FIG. 2

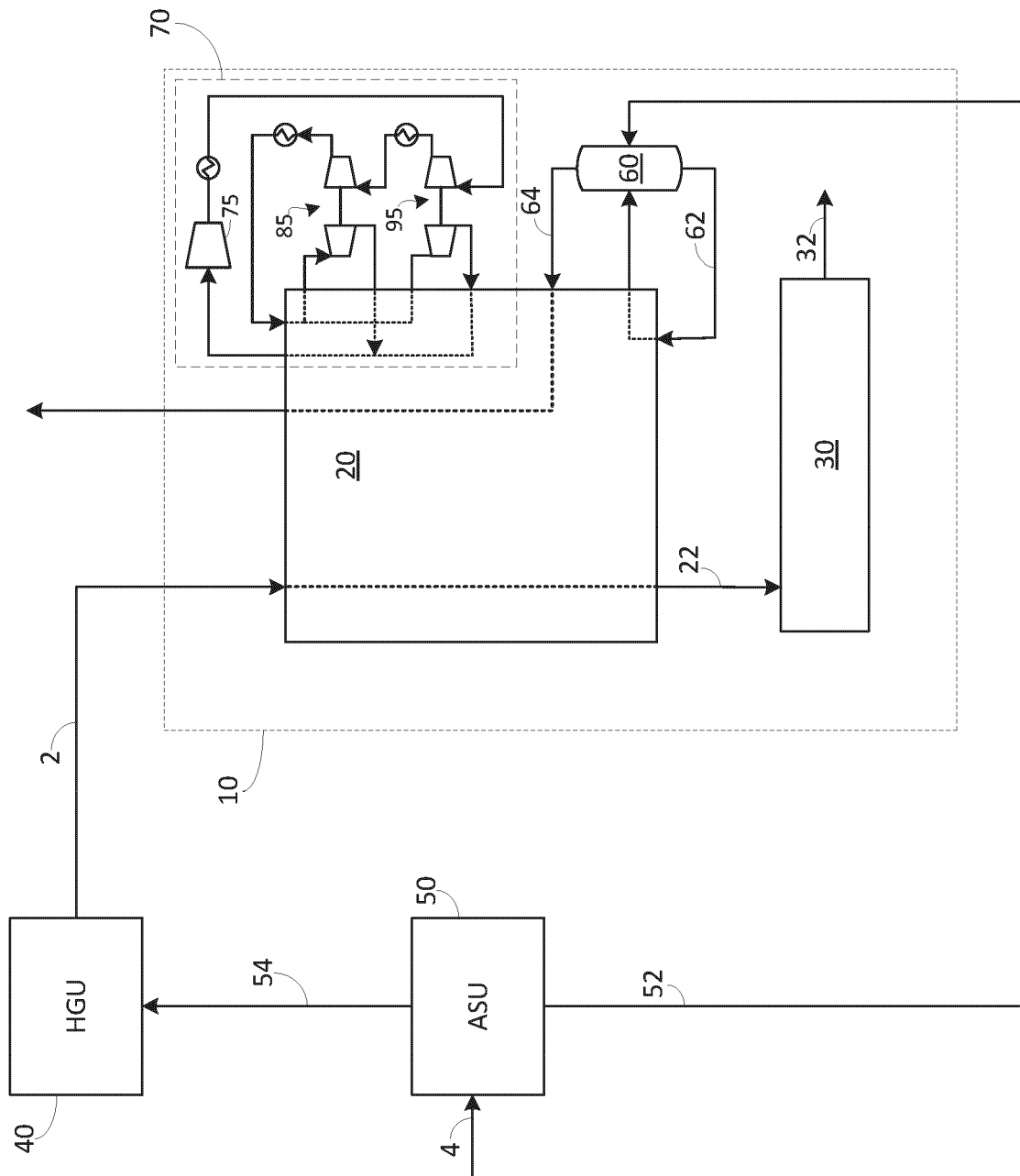


FIG. 3

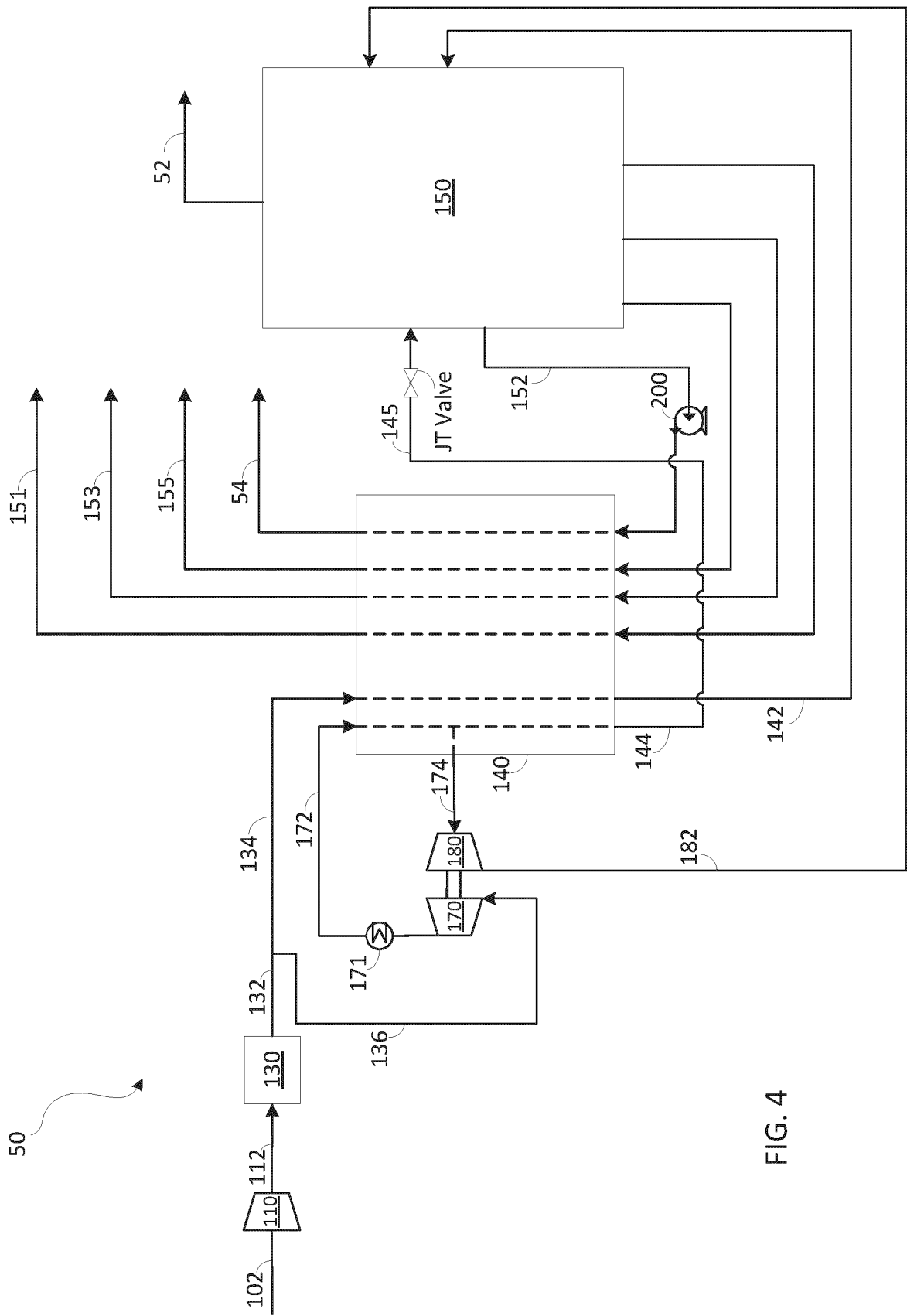


FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 63295509 [0001]
- US 89695322 [0001]
- US 89696722 [0001]
- US 2983585 A, Smith [0011]
- US 3347055 A, Blanchard [0012]
- JP 2002243360 A [0013]
- WO 3347055 A, Blanchard [0013]
- US 5329776 A [0034]
- US 5475980 A [0035]

Non-patent literature cited in the description

- **QUACK.** Conceptual Design of a High Efficiency Large Capacity Hydrogen Liquefier. *Adv. Cryog. Eng., Proc. CEC, Madison 2001, AIP*, vol. 613, 255-263 [0014] [0015]