



(11)

EP 3 163 235 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.05.2017 Bulletin 2017/18

(51) Int Cl.:
F25J 1/00 (2006.01) F25J 1/02 (2006.01)

(21) Application number: **15003068.2**

(22) Date of filing: **27.10.2015**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

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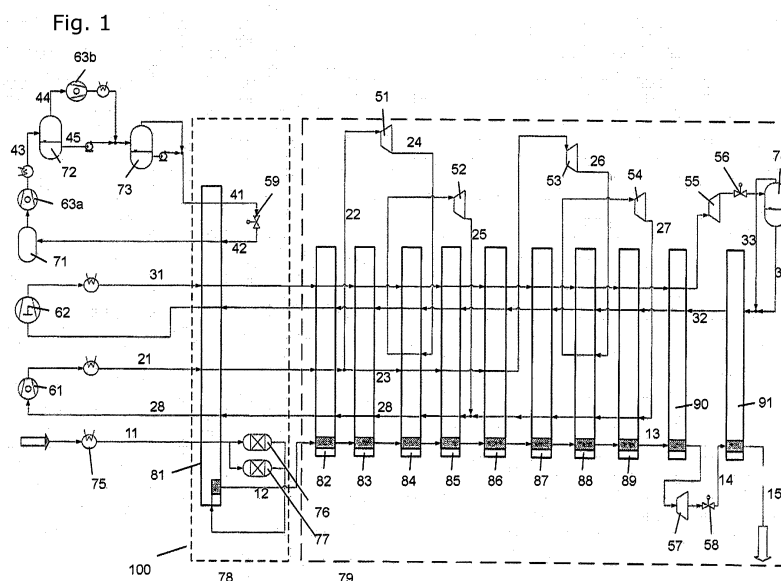
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(54) **NOVEL CASCADE PROCESS FOR COOLING AND LIQUEFYING HYDROGEN IN LARGE-SCALE**

(57) The present invention relates to a method for liquefying hydrogen in large-scale comprising the steps of: providing a feed gas stream comprising hydrogen, precooling the feed gas stream to an intermediate temperature yielding a precooled feed gas stream, cooling the precooled feed gas stream to a temperature of below the critical temperature of hydrogen yielding a liquid product stream comprising hydrogen. According to the invention, the precooled feed gas stream is cooled to a first

temperature in a first cooling step by a first closed cooling cycle with a first refrigerant stream consisting of or comprising neon and/or hydrogen, and that the cooled feed gas stream is further cooled from the first temperature to temperature below the critical temperature of hydrogen in a second cooling step by a second closed cooling cycle with a second refrigerant stream comprising or consisting of hydrogen and/or helium



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Description

[0001] The present invention relates to a method for liquefying hydrogen in large-scale.

[0002] The method comprises the steps of: providing a feed gas stream comprising hydrogen, wherein the feed gas stream is characterized by an initial temperature and a pressure of at least 15 bar(a), precooling the feed gas stream to an intermediate temperature in a precooling step yielding a precooled feed gas stream, wherein particularly the intermediate temperature is in the range of 70 K to 150 K, and cooling the precooled feed gas stream to a temperature below the critical temperature of hydrogen, particularly below 24 K, more particular below 21.15 K, yielding a liquid product stream comprising hydrogen.

[0003] The known technology of hydrogen liquefaction is primarily based on process technology for small-scale industrial hydrogen liquefaction plants with a production capacity typically up to 10 tpd (tons per day) LH2 (for example, the Linde Leuna plant, a hydrogen liquefier with 5 tpd capacity). The hydrogen feed is produced outside the battery limit of the plant from a methane steam reformer or an electrolyser and fed to the liquefaction plant with a typical feed pressure between 15 bar(a) and 30 bar(a). The evaporation of a liquid nitrogen stream at typically 78 K, the nitrogen saturation temperature for 1.1 bar(a), is used to precool the hydrogen feed from ambient temperature to about 80 K in an aluminum-brazed plate-fin heat exchanger. After this step, the hydrogen feed is conducted through a purifier to remove residual impurities, mainly nitrogen, in an absorber vessel. After the purification at 80 K, the hydrogen feed is allowed to pass through additional plate-fin heat exchanger passages filled with catalyst, typically hydrous ferric oxide, for the ortho to para hydrogen conversion. The feed is then again cooled down to about 80 K by the means of liquid nitrogen.

[0004] The final cooling and liquefaction of the hydrogen feed, from about 80 K to the state of saturated or subcooled liquid, is provided by the means of a closed hydrogen Claude loop with typically between one and three cooling strings with turbines expanding the gas from a high pressure (HP) to medium pressure (MP) to provide refrigeration at different temperature levels. A third or the coldest high-pressure refrigeration stream is expanded in a Joule-Thomson valve to a low pressure level (LP) as two-phase gas-liquid stream at the cold end to provide cooling at temperatures below the liquid hydrogen feed stream. The hydrogen feed stream is expanded in a Joule-Thomson valve from supercritical pressure to the desired storage pressure e.g. 1.1 bar(a) (20.5 K), before being stored in a storage tank. The entire refrigeration and liquefaction process is installed within one vacuum insulated cold box. One, two or more hydrogen compressors, particularly reciprocating pistons, are employed at ambient temperature to compress the respective LP and MP hydrogen refrigerant to the HP level before entering the cold-box and being precooled by the warming LP and MP hydrogen in a closed cycle.

[0005] Conceptual process designs for larger hydrogen liquefaction plants, with a production capacity of approximately up to 50 tpd, have been published: in Ohlig et al. ("Hydrogen, 4. Liquefaction" Ullmann's Encyclopedia of Industrial Chemistry, edited by F. Ullmann, Wiley-VCH Verlag, 2013), a closed nitrogen expander refrigeration loop has been proposed as a precooling stage for the hydrogen feed. An improved hydrogen Claude cycle is used for the refrigeration and liquefaction of the hydrogen feed. Patents EP 0342250 and JP H 09303954 describe hydrogen liquefaction using neon in a closed-cycle. In EP 0342250, an open nitrogen stream is used as additional precooling, wherein hydrogen is expanded into the two-phase region with a dense-fluid expander (piston). In JP H 09303954, the hydrogen feed is only cooled via a closed neon cycle. Ortho-para catalytic conversion is carried out as described above and additionally in two isothermal converters within a liquid nitrogen and a liquid neon bath, respectively. Similarly to EP 0342250, the final expansion of the hydrogen feed results in a two-phase fluid. The saturated liquid product is separated in a phase separator while the produced flash gas is warmed up to ambient temperature and compressed together with the feed hydrogen.

[0006] Further known technology are single mixed-refrigerant cooling cycles for industrial gas applications different to hydrogen liquefaction, namely the liquefaction of natural gas (LNG), such as patents US 4,033,735, US 5,657,643 and in Bauer (StarLNG (TM): a Family of Small-to-Mid-Scale LNG Processes, Conference paper, 9th Annual Global LNG Tech Summit 2014: March 2014). These mixed-refrigerants are typically composed of 5 to 7 fluid components to liquefy a natural gas feed from ambient temperature to approximately 120 K. In the IDEALHY study (2012, <http://www.idealhy.eu>), a hydrogen liquefaction process with a mixed-refrigerant cycle with up to seven fluid components is used as a method for precooling the hydrogen down to 132 K. An additional closed-loop Brayton cycle with a 75-25 mol.% helium-neon mixture cools the hydrogen feed stream before the latter is expanded into the two-phase region, similarly to EP 0342250 and JP H 09303954.

[0007] However, the hydrogen feed obtained by the above described methods generates a high fraction of flash gas after the expansion from supercritical to storage pressure, thus requiring an additional recycle compressor at ambient temperature.

[0008] An additional technical difficulty in the up scaled hydrogen liquefiers is the design of efficient turbo-expanders and compressors in the refrigeration cycle. For liquefaction rates above 50 tpd, the hydrogen refrigeration cycle design in the prior art is practically limited through the maximal volumetric flow (frame size) of available reciprocating compressors. Two or three very large reciprocating compressors running in parallel can be operated and maintained. However, a higher number of parallel running large machines is not industrially viable due to economical and operational disad-

vantages e.g. increased installation costs, additional land requirements, high plant maintenance complexity and down-times. This is also the case for helium refrigeration cycles, because of the limited maximal capacity of helium reciprocating compressors and the low isentropic efficiencies of available helium screw-compressors. Turbo-compressors allow for higher volumetric suction flows. However, at suction temperatures close to ambient, stage pressure ratios for light gases such as helium and hydrogen are low for blade tip speeds that are feasible today. Multi-stage turbo-compressors are designed with up to 6 or 8 stages. Thus, the pressure ratios in cold refrigeration cycles containing pure helium or hydrogen require turbo-compressors with an unfavourable or even not viable high number of compressor stages.

[0009] For the cold refrigeration cycle, turbo-expanders with high isentropic efficiencies which are designed with energy recovery, e.g. via turbo-generators or booster compressors, are crucial to increase the overall process efficiency. However, energy and cost efficient turbo-expanders are currently limited by feasible rotational speeds and available frame-sizes.

[0010] Currently known closed-loop precooling cycles for hydrogen liquefiers show deficiencies in either energy-efficiency or capital costs (high process complexity). Closed-loop nitrogen expander cycles as described in Ohlig et al. can reach cooling temperatures below 80 K but are characterized by a relatively high number of additional rotating machines and a significantly lower thermodynamic efficiency compared to single mixed-refrigerant cycles.

[0011] Additionally, known mixed-refrigerant cycles for natural gas or hydrogen liquefaction applications can increase precooling efficiency but are typically designed for relatively high precooling temperatures (≥ 120 K), thus shifting the generation of the required cooling duty to the colder, more inefficient refrigeration cycle in a hydrogen liquefier. Additionally, common refrigerant mixtures have been designed with a high number of fluid components e.g. 5 to 7. These have to be regularly imported to the hydrogen liquefier plant for inventory make-up and require additional storage tanks for each component, thus increasing operational complexity and handling.

[0012] Furthermore, refrigeration fluids providing cooling down to temperatures below approximately 60 K and close to the liquid hydrogen product are limited to hydrogen, helium and neon as well as to mixtures of these. Both normal boiling point (27.1 K) and melting point (24.6 K) of neon are higher than the normal boiling point of hydrogen (20.3 K). Hence, in order to avoid freeze-out within the process equipment, cold refrigeration cycles with pure neon or mixtures with neon are not designed to reach cooling temperatures close or lower than 24.6 K.

[0013] Thus, it is the objective of the present invention to provide an efficient and economic method for liquefying hydrogen that is particularly suitable for large scales.

[0014] The objective is solved by the method according to claim 1.

[0015] According thereto, the precooled feed gas stream is cooled to a first temperature in a first cooling step, particularly in a first cooling zone, by a first closed cooling cycle with a first refrigerant stream consisting of or comprising neon and/or hydrogen, wherein the first refrigerant stream is expanded, thereby producing cold, and the cooled feed gas stream is further cooled from the first temperature to a temperature below the critical temperature of hydrogen, particularly below 24 K, more particular below 21.15 K, in a second cooling step, particularly in a second cooling zone, by a second closed cooling cycle with a second refrigerant stream comprising or consisting of hydrogen and/or helium, wherein the second refrigerant stream is expanded, thereby producing cold.

[0016] Advantageously, the method of the invention enables a thermodynamically and economically efficient liquefaction of hydrogen on a large-scale, with production capacities of up to 10 to 20 times above conventional liquefiers e.g. 150 tpd per liquefier train. Specific energy consumption, and thus operational costs, is significantly reduced compared to prior concepts described above, while utilizing process equipment and frame sizes that are commercially available today. Compared to prior published studies for large-scale liquefiers, the method of the invention requires significantly reduced rotating equipment count and a lower number of imported refrigerant fluids, thus reducing the plant operational complexity and capital costs, as well as increasing plant availability and maintainability.

[0017] Particularly, the feed gas stream is characterized by hydrogen concentration of at least 99.99 Vol. %

[0018] Preferably, ortho hydrogen comprised within the feed gas stream (about 75%) is converted to higher para hydrogen fractions preferably before liquefaction of the feed gas stream to avoid that the exothermic ortho to para reaction takes place in the liquid product possibly resulting in an undesired partial vaporization of the liquid hydrogen product during storage and transport.

[0019] In certain embodiments, the feed gas stream is precooled to the intermediate temperature in a precooling zone.

[0020] In certain embodiments, the first refrigerant stream and/or the second refrigerant stream is precooled to the intermediate temperature, particularly in the above-mentioned precooling zone.

[0021] In certain embodiments, the first temperature lies in the range of 24.6 K to 44.5 K, particularly in the range of 26 K to 33 K.

[0022] In certain embodiments, the first refrigerant stream comprises neon in the range of 0 mol. % to 100 mol. %. In certain embodiments, the first refrigerant stream comprises neon in the range of 80 mol. % to 100 mol. %. In certain embodiments, the first refrigerant stream consists of neon. In certain embodiments, the first refrigerant stream comprises or consists of 50 mol. % to 100 mol. % neon, and optionally hydrogen, particularly in a concentration up to 50 mol. %. In certain embodiments, the first refrigerant stream comprises or consists of 20 mol. % to 100 mol. % neon, and optionally

hydrogen, particularly up to 80 mol. %. In certain embodiments, the first refrigerant stream comprises 30 mol. % to 70 mol. % neon, and optionally hydrogen, particularly up to 70 mol. %. In certain embodiments, the first refrigerant stream consists of 30 mol. % to 70 mol. % neon and hydrogen. In certain embodiments, the first refrigerant stream comprises 40 mol. % to 60 mol. % neon, and optionally hydrogen, particularly up to 60 mol. %. In certain embodiments, the first refrigerant stream consists of 40 mol. % to 60 mol. % neon and hydrogen. In certain embodiments, the first refrigerant stream comprises 80 mol. % to 100 mol. % hydrogen and neon, particularly up to 20 mol. %. In certain embodiments, the first refrigerant stream comprises 80 mol. % to 90 mol. % hydrogen and 10 mol. % to 20 mol. % neon. In certain embodiments, the first refrigerant stream consists of 80 mol. % to 90 mol. % hydrogen and neon.

[0023] In certain embodiments, the intermediate temperature is in the range of 70 K to 120 K. In certain embodiments, the intermediate temperature is in the range of 80 K to 120 K. In certain embodiments, the intermediate temperature is in the range of 85 K to 120 K. In certain embodiments, the intermediate is in the range of 90 K to 120 K. In certain embodiments, the intermediate temperature is around 100 K. In certain embodiments, the intermediate temperature is in the range of 120 K to 140 K. In certain embodiments, the precooling zone is located within an at least one precooling heat exchanger or a precooling block of a heat exchanger. In certain embodiments, the at least one precooling heat exchanger is a plate fin heat exchanger.

[0024] In certain embodiments, the feed gas stream is precooled to an intermediate temperature in the range of 80 K to 120 K, particularly 100 K, yielding the precooled feed gas stream, and the precooled feed gas stream is brought into contact with a catalyst being able to catalyse the ortho to para conversion of hydrogen, particularly before the first cooling step. In certain embodiments, the catalyst is or comprises hydrous ferric oxide. In certain embodiments, the catalyst is arranged within a heat exchanger, particularly within the at least one precooling heat exchanger or the precooling block, in which the feed gas stream is precooled.

[0025] In certain embodiments, the feed gas stream is precooled in the precooling step by a closed precooling cycle with a third refrigerant stream, wherein the third refrigerant stream is expanded, thereby producing cold, and the third refrigerant stream comprises or consists of nitrogen, a mixture of C₁-C₅ hydrocarbons, or a mixture of nitrogen and at least one C₁-C₅ hydrocarbons.

[0026] In certain embodiments, the third refrigerant stream consist of a liquid nitrogen stream, wherein the liquid nitrogen stream is expanded or evaporated, thereby cooled, particularly to a temperature in the range of 70 K to 80K, and the cool expanded or evaporated nitrogen stream and the feed gas stream, the first refrigerant stream and/or the second refrigerant stream are guided such that heat can indirectly be transferred between the expanded or evaporated nitrogen stream and any one or all of the aforementioned streams, thereby particularly cooling the feed gas stream, the first refrigerant stream and/or the second refrigerant stream, particularly in the above mentioned at least one precooling heat exchanger or precooling block. In certain embodiments, the expanded or evaporated nitrogen refrigerant stream is released into the environment after cooling the above-mentioned stream. In certain embodiments, the liquid nitrogen stream is expanded or evaporated, particularly in a turbo expander and a throttle valve, and compressed in a closed cycle. In certain embodiments, the expanded or evaporated nitrogen stream is guided against the feed gas stream and/or the first refrigerant stream in the precooling zone.

[0027] In certain embodiments, the third refrigerant stream consists of a liquid natural gas stream, wherein the liquid natural gas stream is expanded or evaporated, thereby cooled, particularly to a temperature in the range of 110 K to 150 K, and the expanded or evaporated natural gas stream and the feed gas stream, the first refrigerant stream and/or the second refrigerant stream are guided such that heat can indirectly be transferred between the expanded natural gas stream and any one or all of the aforementioned streams, thereby particularly cooling the feed gas stream, the first refrigerant stream and/or the second refrigerant stream, particularly in the above mentioned at least one precooling heat exchanger or precooling block. After cooling the aforementioned stream, the expanded or evaporated natural gas stream can be guided into a supply line or to a process consuming natural gas. In certain embodiments, the expanded or evaporated natural gas stream is guided against the feed gas stream and/or the first refrigerant stream in the precooling zone.

[0028] In certain embodiments, the C₁-C₅ hydrocarbon is selected from the group comprised of methane, ethane, ethylene, n-butane, isobutane, propane, propylene, n-pentane, isopentane and 1-butene.

[0029] In certain embodiments, the third refrigerant is a single-mixed refrigerant comprising or consisting of four components, wherein a first component is nitrogen, or optionally nitrogen in a mixture with neon and/or argon, a second component is methane, a third component is ethane or ethylene, and a fourth component is n-butane, isobutane, 1-butene, propane, propylene, n-pentane or isopentane.

[0030] In certain embodiments, the third refrigerant comprises a fifth component, wherein the fifth component is n-butane, isobutane, 1-butene, propane, propylene, n-pentane or isopentane provided the fifth component is different from the fourth component, e.g. the fifth component can be n-butane, isobutane, propane, propylene or n-pentane if the fourth component is isopentane.

[0031] In certain embodiments, the third refrigerant comprises a sixth component, wherein the sixth component is n-butane, isobutane, propane, propylene, n-pentane or isopentane provided the sixth component differs from the fourth

component and fifth component, e.g. the sixth component can be isobutane, propane, propylene or n-pentane if the fourth component is isopentane and the fifth component is n-butane.

[0032] In certain embodiments, the third component is ethane. Such composition of the third refrigerant is particularly useful if the intermediate temperature to be achieved in the precooling step is below or equal to 100 K. In certain embodiments, third component is ethylene. Such composition of the third refrigerant is particularly useful if the intermediate temperature to be achieved in the precooling step is above 100 K.

[0033] In certain embodiments, the fourth component and optionally the fifth component is, isobutane, 1-butene, propane, propylene or isopentane, provided that the fifth component is different from the fourth component. Such composition of the third refrigerant is particularly useful if the intermediate temperature to be achieved in the precooling step is below 100 K.

[0034] In certain embodiments, the first component is nitrogen in a mixture with neon and/or argon, a second component is methane, a third component is ethane or ethylene, and a fourth component is n-butane, isobutane, 1-butene propane, propylene, n-pentane or isopentane. Such composition of the third refrigerant is particularly useful if the intermediate temperature to be achieved in the precooling step is below 100 K

[0035] In certain embodiments, the third refrigerant comprises 18 mol. % to 23 mol. % nitrogen, and/or 27 mol. % to 29 mol. % methane, and/or 24 mol. % to 37 mol. % ethane, and/or 18 mol. % to 24 mol. % isopentane or isobutane, provided that the sum of the concentrations of the above-mentioned components does not exceed 100 mol %. Such composition of the third refrigerant is particularly useful if the intermediate temperature to be achieved in the precooling step is around 100 K.

[0036] In certain embodiments, the third refrigerant consists of 18 mol. % nitrogen, 27 mol. % methane, 37 mol. % ethane and 18 mol. % isopentane. Such composition of the third refrigerant is particularly useful if the intermediate temperature to be achieved in the precooling step is around 100 K.

[0037] In certain embodiments, the third refrigerant consists of 23 mol. % nitrogen, 29 mol. % methane, 24 mol. % ethane, and to 24 mol. % isobutane. Such composition of the third refrigerant stream is particularly useful if the intermediate temperature to be achieved in the precooling step is around 100 K.

[0038] In certain embodiments, residual impurities, particularly nitrogen, and/or oxygen are removed from the precooled feed gas stream before contacting the precooled feed stream with the above-mentioned catalyst and/or before the intermediate temperature is below 80 K, particularly by means of an adsorber. In certain embodiments, an adiabatic or isothermal ortho-para catalytic converter vessel is placed directly downstream or within the adsorber, wherein normal-hydrogen comprised within the feed gas stream is converted in a first step to a para-content near the equilibrium at the intermediate temperature, e.g. 39 % at 100 K.

[0039] In certain embodiments, the first cooling cycle comprises the steps of:

- providing the first refrigerant stream with a first pressure,
- separating the first refrigerant stream at least into a first partial stream and a second partial stream,
- expanding the first partial stream in a first expansion device to a first intermediate pressure yielding an partially expanded first partial stream and/or to a second pressure yielding an expanded first partial stream,
- expanding the second partial stream to a third pressure in a second expansion device yielding an expanded second partial stream,
- guiding the expanded second partial stream and the precooled feed gas stream such that heat can indirectly be transferred between the expanded second partial stream and the precooled feed gas stream, thereby particularly cooling the feed gas stream to the first temperature, particularly in the first cooling zone,
- merging the partially expanded first partial stream or the expanded first partial stream with the expanded second partial stream after being guided with the precooled feed gas stream yielding an expanded first refrigerant stream, and
- compressing the expanded first refrigerant stream to the first pressure yielding the first refrigerant stream.

[0040] The term "indirectly heat transfer" in the context of the present invention refers to the heat transfer between at least two fluid streams that are spatially separated such that the at least two fluid streams do not merge or mix but are in thermal contact, e.g. two fluid streams are guided through two cavities, for example of a plate heat exchanger, wherein the cavities are separated from each other by a wall or plate, and both streams do not mix, but heat can be transferred via the wall or the plate.

[0041] Alternatively, the expanded second partial stream is compressed to a pressure close or equal to the first intermediate pressure, and the partially expanded first partial stream is guided into or unified with the second partial stream after compression to the pressure close or equal to the first intermediate pressure yielding a partially expanded first refrigerant stream, which is then particularly compressed to the first pressure yielding the first refrigerant stream.

[0042] Particularly, a first pressure is close to a second pressure if both pressures do not differ more the 10 % or not more than 5 bar(a), 4 bar(a), 3 bar(a), 2 bar(a) or 1 bar(a) from each other.

[0043] In certain embodiments, the first refrigerant stream is precooled by the third refrigerant stream.

[0044] In certain embodiments, the expanded first refrigerant stream and the precooled feed gas stream are guided such that heat can indirectly be transferred between the streams, thereby particularly cooling the precooled feed gas stream, particularly in the first cooling zone. In certain embodiments, the expanded first refrigerant and the second partial stream and/or the first refrigerant stream are guided such that heat can be transferred between the expanded first refrigerant stream and the second partial stream and/or the first refrigerant stream, thereby particularly cooling the second partial stream and/or the first refrigerant stream, particularly in the first cooling zone. Advantageously, the partially expanded first partial stream or the expanded first partial stream within the expanded first refrigerant stream provides additional cooling duty to cool the aforementioned streams. In certain embodiments, the expanded first refrigerant stream is guided against the second partial stream, the precooled feed gas stream and/or the first refrigerant stream in the first cooling zone such that heat can indirectly be transferred between the expanded first refrigerant stream and the precooled feed gas stream and/or the first refrigerant stream.

[0045] In certain embodiments, the first expansion device comprises at least one turbo-expander. In certain embodiments, the first expansion device comprises at least two turbo-expanders, wherein particularly the first partial stream is expanded in a first turbo-expander to the first intermediate pressure yielding the partially expanded first partial stream, and the partially expanded first partial stream is expanded in a second turbo-expander to the second pressure.

[0046] In certain embodiments, the partially expanded first partial stream and the second partial stream are guided such that heat can be indirectly transferred between the partially expanded first partial stream and the second partial stream, wherein particularly the second partial stream is cooled. In certain embodiments, the partially expanded first partial stream is guided against the second partial stream in the first cooling zone such that heat can indirectly be transferred between the partially expanded first partial stream and the second partial stream, thereby particularly cooling the second partial stream.

[0047] In certain embodiments, the second partial stream is expanded in a second expansion device to a second intermediate pressure yielding a partially expanded second partial stream, the partially expanded second partial stream and the second refrigerant stream and/or the precooled feed gas stream are guided such that heat can be transferred between the partially expanded second partial stream and the second refrigerant stream and/or the precooled feed gas stream, thereby particularly cooling the second refrigerant stream and/or the precooled feed gas stream, and the partially expanded second partial stream is expanded to the second pressure yielding the expanded partial stream. In certain embodiments, the partially expanded second partial stream is guided against the second refrigerant stream and/or the precooled feed gas stream in the first cooling zone such that heat can indirectly be transferred between the partially expanded second partial stream and the second refrigerant stream and/or the precooled feed gas stream.

[0048] In certain embodiments, the second expansion device comprises at least one turbo-expander. In certain embodiments, the second expansion device comprises at least two turbo-expanders, wherein particularly the second partial stream is expanded in a third turbo-expander to the second intermediate pressure yielding the partially expanded second partial stream, the partially expanded second partial stream is expanded in a fourth turbo-expander to the third pressure.

[0049] In certain embodiments, the first cooling zone is located within at least one cooling heat exchanger or a cooling block of a heat exchanger, through which particularly the expanded second partial and the precooled feed stream, the first partial stream, the second partial stream, the first refrigerant stream and/or the second refrigerant stream are guided. In certain embodiments, the at least one heat exchanger comprises a catalyst being able to catalyse the ortho to para conversion of hydrogen, wherein the precooled feed gas stream is guided through the at least one heat exchanger such that the precooled feed gas stream contacts the catalyst. In certain embodiments, the at least one cooling heat exchanger is a plate heat exchanger.

[0050] In certain embodiments, the first refrigerant stream consists of neon, the first pressure is in the range of 5 bar(a) to 40 bar(a) and, particularly in the range of 10 bar(a) to 30 bar(a), and the second pressure and/or third pressure is in the range of 1.013 bar(a) to 10 bar(a), particularly in the range of 1.3 bar(a) and 4 bar(a), particularly provided that the first refrigerant is precooled to a precooling temperature in the range of 70 K to 120 K, particularly 100 K.

[0051] In certain embodiments, the first refrigerant stream consists of neon, the first pressure is in the range of 4 bar(a) to 10 bar(a) and the second pressure and/or third pressure is in the range of 0.7 bar(a) to 1.013 bar(a), particularly provided that the first refrigerant is precooled to a precooling temperature in the range of 70 K to 120 K, particularly 100 K.

[0052] In certain embodiments, the first refrigerant stream comprises or consists of 20 mol. % to 100 mol. % neon, particularly 50 mol.% to 100 mol.% neon, more particular 30 mol.% to 70 mol. % neon, even more particular 40 mol.% to 60 mol.% neon, and optionally hydrogen, the first pressure is in the range of 5 bar(a) and 75 bar(a), particularly 10 bar(a) to 60 bar(a), the first intermediate pressure is between the first pressure and third pressure, and the second and/or third pressure is in the range of 0.7 bar(a) and 13 bar(a), particularly provided that the first refrigerant is precooled to a precooling temperature in the range of 70 K to 120 K, particularly 100 K.

[0053] In certain embodiments, the first refrigerant stream comprises or consists of 80 mol. % to 100 mol. % hydrogen, particularly 80 mol. % to 90 mol. % hydrogen, and optionally neon, particularly 10 mol. % to 20 mol. % neon, the first pressure is in the range of 20 bar(a) and 75 bar(a), and the second and/or the third pressure is in the range of 0.7 bar(a) to 13 bar(a), particularly provided that the first refrigerant is precooled to a precooling temperature in the range of 70 K

to 120 K, particularly 100 K.

[0054] Advantageously, if a higher neon mole fraction is present in the first refrigerant stream (higher molecular weight), a favourable turbo machine design particularly in terms of feasible stage pressure ratio in turbo-compressor or turbo-expanders can be applied.

[0055] Advantageously, if a higher hydrogen mole fraction is present in the first refrigerant stream (lower molecular weight), a higher low pressure level is feasible at the discharge of the coldest turbine for the same cooling temperature. Additionally, a hydrogen is characterized by a significantly lower heat capacity ratio compared to neon (and helium), resulting in lower compressor discharge temperatures. Higher energy-efficiency can be realized

[0056] In certain embodiments, the expanded second partial stream is characterized by a temperature in the range of 26 K to 33 K, wherein particularly the precooled feed gas stream and/or the second refrigerant stream is cooled by the expanded second partial stream close to those temperatures. In certain embodiments, the expanded first refrigerant stream is compressed with a suction temperature close to ambient temperature, or in the range of 230 K to 313 K, or in cold-compressors at a temperature in the range of 80 K to 120 K, or in the range of 120 K to 230 K, particularly above the precooling or intermediate temperature, e.g. 150 K. In certain embodiments, the expanded first refrigerant stream is compressed in a multi stage compressor comprising at least three compressor stages with intercooling.

[0057] In certain embodiments, the partially expanded first refrigerant stream and/or the expanded first refrigerant stream is compressed in at least one multi-stage reciprocating compressors, particularly in two or three multi-stage reciprocating compressors running in parallel configuration e.g. 2 x 100% (capacity) or 2 x 100% (capacity) plus 1 x 50% (capacity), or in two 100 % (capacity) multi-stage reciprocating compressors and one 50 % (capacity) reciprocating compressor.

[0058] In certain embodiments, the first refrigerant stream is separated in the first partial and the second partial stream as described above, and additionally in a third partial stream and optionally in a fourth partial stream, wherein the third partial stream is expanded in a sixth expansion device to a third intermediate pressure yielding a partially expanded third partial stream or to the second pressure yielding an expanded third partial stream, and optionally the fourth partial stream is expanded in a seventh expansion device to a fourth intermediate pressure yielding a partially expanded fourth partial stream or to the second pressure yielding an expanded fourth partial stream, and the partially expanded third partial stream or the expanded third partial stream is guided into or unified with the partially expanded second partial stream, the expanded second partial stream or the partially expanded first refrigerant stream, and optionally the partially expanded fourth partial stream or the expanded fourth partial stream is guided into or unified with the partially expanded second partial stream, the expanded second partial stream or the partially expanded first refrigerant stream. Advantageously, the partially or fully expanded third and/or fourth partial stream within the expanded second partial stream provides additional cooling duty to cool the aforementioned streams to be cooled.

[0059] In certain embodiments, the expanded second partial stream is compressed from the third pressure to the pressure close or equal to the first intermediate pressure by means of at least one reciprocating piston compressor, particularly two or three reciprocating piston compressors, particularly at any suction temperature. Particularly for cold-compression of the expanded second partial stream, particularly at a suction temperature in the range of 80 K to 120 K, or in the range of 120 K to 230 K, one or two multi stage turbo-compressor are preferred.

[0060] In certain embodiments, the first refrigerant stream comprises 5 mol. % to 100 mol. % neon, and the expanded first refrigerant stream and/or the expanded second partial stream is compressed with a suction temperature close to ambient temperature, or in the range of 230 K to 313 K in one or two multi-stage turbo compressors in series.

[0061] In certain embodiments, the first refrigerant stream comprises 20 mol. % to 100 mol. % neon, and the partially expanded first refrigerant stream, the expanded first refrigerant stream and/or the partially expanded second partial stream is compressed with a suction temperature close to ambient temperature, or in the range of 230 K to 313 K in one multi-stage turbo compressor.

[0062] In certain embodiments, the sixth and/or the seventh expansion device comprise at least one turbo-expander.

[0063] Generally, compressing an expanded refrigerant stream, such as the above mentioned expanded first refrigerant stream, at a temperature below the ambient temperature, particularly at temperature in the range of 80 K to 230 K, has the advantage that the volume of the stream to be compressed is reduced, thereby smaller compressors and smaller capital costs are required. Further, advantageously, less compressor stages are required.

[0064] In certain embodiments, the second cooling cycle comprises the steps of:

- providing the second refrigerant stream with a fourth pressure,
- expanding the second refrigerant stream in a third expansion device to a fifth pressure yielding an expanded second refrigerant stream that is particularly characterized by a temperature in the range of 16 K and 30 K, more particular in the range of 20 K and 24 K, depending on the storage pressure of the liquid hydrogen product
- guiding the expanded second refrigerant stream and the cooled feed gas stream in the second cooling zone such that heat can indirectly be transferred between the expanded second refrigerant stream and the cooled feed gas stream, thereby liquefying the cooled feed gas stream to the liquid product stream,

- compressing the expanded second refrigerant stream to the fourth pressure yielding the second refrigerant stream.

[0065] In certain embodiments, the second refrigerant stream is precooled by the third refrigerant stream.

[0066] In certain embodiments, the third expansion device is a turbo-expander or piston-expander, a throttle valve or a combination of a turbo-expander or piston-expander and a throttle valve.

[0067] In certain embodiments, the expanded second refrigerant and the second refrigerant stream are guided in the second cooling zone such that heat can indirectly be transferred between the expanded second refrigerant and the second refrigerant stream, thereby particularly cooling the second refrigerant stream. In certain embodiments, the expanded second refrigerant stream and the first refrigerant stream and/or the second partial stream are guided in the second cooling zone such that heat can indirectly be transferred between the expanded second refrigerant stream and the first refrigerant stream and/or the second partial stream, thereby particularly cooling the first refrigerant stream and/or warming the second partial stream. In certain embodiments, the expanded second refrigerant stream is guided against the cooled feed gas stream, the first refrigerant stream, the second refrigerant stream and/or the second partial stream such that heat can indirectly be transferred between the expanded second refrigerant stream and the cooled feed gas stream, the first refrigerant stream, the second refrigerant stream and/or the second partial stream, thereby particularly liquefying the cooled feed gas stream and/or cooling the first refrigerant stream and/or the second refrigerant stream and/or warming the second partial stream, particularly in the second cooling zone.

[0068] In certain embodiments, the second refrigerant comprises essentially hydrogen, the fourth pressure is equal or above 15 bar(a), preferably between 15 bar(a) and 30 bar(a) and the fifth pressure (particularly after expansion device and throttle valve) is below the critical pressure of hydrogen, preferably between 1.0 bar(a) and 2 bar(a), wherein particularly the expanded second refrigerant is characterized by a temperature in the range of 18 K and 30 K, particularly after expansion in a turbo-expander or piston expander and a throttle valve, particularly in the range of 20 K and 24 K.

[0069] In certain embodiments, the second refrigerant comprises essentially helium, the fourth pressure is above 20 bar(a), preferably between 20 bar(a) and 100 bar(a), more preferably between 50 bar(a) and 70 bar(a), and the fifth pressure is above 5 bar(a), preferably in the range of 12 bar(a) and 25 bar(a). Advantageously, such second refrigerant can directly be expanded to the fifth pressure in a single turbo-expander without formation of a two-phase fluid, whereby additionally a phase separator can be saved. Advantageously, in this way, a low hydrogen feed storage temperature can be reached, particularly below 20 K. In certain embodiments, the second refrigerant stream comprises essentially helium, and the expanded second refrigerant stream is compressed in an ionic liquid piston compressor.

[0070] An ionic liquid piston compressor in the context of the present specification particularly refers to a compressor, in which at least one or all conventional metal pistons are replaced by a nearly incompressible ionic liquid, wherein particularly the gas is compressed in the cylinder of the compressor by the up-and-down motion of the liquid column, similar to the reciprocating motion of an ordinary piston.

[0071] In certain embodiments, the second refrigerant stream comprises essentially hydrogen and is expanded to an intermediate pressure, at which a two-phase flow within a turbo-expander is avoided, e.g. in the range of 5 bar(a) to 15 bar(a), and the partially expanded second refrigerant stream is further expanded in a throttle valve to the fifth pressure. Advantageously, the throttle valve (isenthalpic expansion) is placed at the turbo-expander outlet or a piston expander outlet for expansion into two-phase region to avoid two-phase flow (dry gas expander) within the turbo expander. If the expansion device is designed to allow a two-phase fluid at the expander outlet, e.g. wet turbine / piston-expander, then throttle valve might not be required.

[0072] In certain embodiments, the expanded second refrigerant is separated into a vapour phase and a liquid phase, wherein both phases are separately or together guided with the above mentioned streams.

[0073] In certain embodiments, the second refrigerant is separated into at least two partial streams, wherein a first partial stream is expanded to the fourth pressure as described above, and a second partial stream is expanded to an intermediate pressure, the expanded first partial stream is compressed to a pressure close or equal to the intermediate pressure, the partially expanded second partial stream is guided into or unified with the first partial stream after compression to the pressure close or equal to the intermediate pressure yielding a partially expanded second refrigerant stream, which is then compressed to the fourth pressure yielding the second refrigerant stream.

[0074] In certain embodiments, the second cooling zone is located within at least one heat exchanger or a block of the at least on cooling heat exchanger, through which particularly the expanded second partial stream and the hydrogen feed stream are guided. In certain embodiments, the at least one heat exchanger or the block of the at least on cooling heat exchanger comprises a catalyst being able to catalyse the ortho to para conversion of hydrogen, wherein the feed gas stream is guided through the at least one heat exchanger or the block of the at least on cooling heat exchanger such that the feed gas stream contact the catalyst.

[0075] In certain embodiments, the second refrigerant is directly replenished by the feed gas stream, particularly after residual impurities have been removed from the feed gas stream as described above.

[0076] In certain embodiments, the second refrigerant stream is separated at least into a first partial stream and a second partial stream, wherein the first partial stream of the second refrigerant stream is expanded to the fifth pressure

yielding an expanded first partial stream of the second refrigerant stream, and the second partial stream of the second refrigerant stream is expanded to an intermediate pressure yielding a partially expanded second partial stream of the second refrigerant stream or to the fifth pressure yielding an expanded second partial stream of the second refrigerant stream, the expanded first partial stream of the second refrigerant stream and the cooled feed gas stream are guided such that heat can indirectly be transferred between the expanded first partial stream of the second refrigerant stream and the cooled feed gas stream, particularly in the second cooling zone, thereby particularly cooling the cooled feed gas stream to a temperature below the critical temperature of hydrogen, particularly below 24 K, and the partially expanded second partial stream or the expanded second partial stream of the second refrigerant is guided into or unified with the expanded first partial stream of the second refrigerant stream. In certain embodiments, the first partial stream of the second refrigerant stream is guided against the cooled feed gas stream in the second cooling zone such that heat can indirectly be transferred between the first partial stream of the second refrigerant stream and the cooled feed gas stream, thereby particularly cooling the cooled feed gas stream.

[0077] In certain embodiments, the second refrigerant stream is further separated into a third and optionally a fourth partial stream, wherein the third, and optionally the fourth partial stream of the second refrigerant stream, is expanded and guided in the same manner as the above-mentioned partially expanded second partial stream or expanded second partial stream of the second refrigerant stream.

[0078] In certain embodiments, the expanded first partial stream of the second refrigerant stream is compressed to a pressure close to the intermediate pressure of the partially expanded second, third or fourth partial stream of the second refrigerant stream yielding a partially expanded first partial stream, and the partially expanded second, third and/or fourth partial stream of the second refrigerant stream are guided into or unified with the partially expanded first partial stream yielding a partially expanded second refrigerant stream, which is then particularly compressed to the fourth pressure yielding the second refrigerant stream.

[0079] In certain embodiments, the expanded second refrigerant stream, the partially expanded second refrigerant stream and/or the expanded first partial stream of the second refrigerant stream is compressed with a compressor suction temperature close to the ambient temperature, or at a temperature in the range of 230 K to 313 K, or at a temperature in the range of 120 K to 230 K, particularly 150 K, or at a temperature in the range of 80 K to 120 K, or a temperature in the range of 30 K to 80 K, particularly after being warmed to the temperature in a heat exchanger. In certain embodiments, the expanded second refrigerant stream, the partially expanded second refrigerant stream and/or the expanded first partial stream of the second refrigerant stream is compressed in a multi stage reciprocating piston compressor with at least two compressor stages, preferably at least three compressor stages, optionally with intercooling, or in an ionic liquid piston compressor. Advantageously, an ionic liquid piston compressor can be employed for compressing the expanded second refrigerant stream if the second refrigerant stream essentially comprises helium. Particularly for cold-compression of the expanded second refrigerant stream, the partially expanded second refrigerant stream and/or the expanded first partial stream of the second refrigerant stream, particularly at a suction temperature in the range of 80 K to 120 K, or in the range of 120 K to 230 K, one or two multi stage turbo-compressor are preferred.

[0080] In certain embodiments, the precooling step comprises the steps of:

- providing the third refrigerant with an sixth pressure,
- expanding the third refrigerant stream in a fourth expansion device to an seventh pressure yielding an expanded third refrigerant stream,
- guiding the expanded third refrigerant stream and the feed gas stream such that heat can indirectly be transferred between the expanded third refrigerant stream and the feed gas stream, thereby particularly precooling the feed gas stream, particularly to the intermediate temperature,
- compressing the expanded third refrigerant to the sixth pressure in a first precooling compressor.

[0081] In certain embodiments, the expanded third refrigerant stream is guided against the feed gas stream in the precooling zone such that heat can indirectly be transferred between the expanded third refrigerant stream and the feed gas stream, thereby precooling the feed gas stream, particularly to the intermediate temperature.

[0082] In certain embodiments, the sixth pressure is above 20 bar(a). In certain embodiments, sixth pressure is in the range of 20 bar(a) to 75 bar(a). In certain embodiments, the sixth pressure is in the range 30 bar(a) to 60 bar(a). In certain embodiments, the seventh pressure is in the range of 1.1 bar(a) to 8 bar(a). In certain embodiments, the expanded third refrigerant stream is characterized by a temperature in the range of 70 K to 150 K, preferably in the range of 70 K to 120 K, more preferable in the range of 80 K to 120 K, most preferable in the range of 90 K to 120 K. In certain embodiments, the expanded third refrigerant stream and the first refrigerant stream and/or the second refrigerant stream and/or the third refrigerant stream are guided such that heat can indirectly be transferred between the expanded third refrigerant stream and the first refrigerant stream and/or the second refrigerant stream and/or the third refrigerant stream, thereby particularly precooling the first refrigerant stream and/or the second refrigerant stream and/or the third refrigerant, particularly in the precooling zone. In certain embodiments, the fourth expansion device is a throttle valve. In certain

embodiments, the expanded third refrigerant stream is guided against the first refrigerant stream and/or the second refrigerant stream and/or the third refrigerant stream in the precooling zone such that heat can indirectly be transferred between the expanded third refrigerant stream and the first refrigerant stream and/or the second refrigerant stream and/or the third refrigerant stream, thereby particularly cooling the first refrigerant stream and/or the second refrigerant stream and/or the third refrigerant stream.

[0083] In certain embodiments, compressing the expanded third refrigerant stream comprises the steps of:

- compressing the expanded third refrigerant stream in a first precooling compressor or a first compressor stage of the first precooling compressor to an intermediate pressure yielding an intercooled third refrigerant stream, wherein the intermediate pressure is between the sixth pressure and the seventh pressure,
- separating the intercooled third refrigerant stream into a mainly liquid third refrigerant stream and a mainly gaseous third refrigerant stream, wherein the mainly liquid third refrigerant stream is pumped up to the sixth pressure, and the mainly gaseous third refrigerant stream is compressed in a second compressor or a second compressor stage of the first precooling compressor to the eighth pressure,
- combining the compressed mainly liquid third refrigerant stream and the compressed mainly gaseous third refrigerant stream to the third refrigerant stream.

[0084] In certain embodiments, the expanded third refrigerant stream is compressed in at least 2 compressor stages or compressors, optionally with intercooling, or if the third refrigerant is compressed in the two phase region with a pump and a phase separator between the compressor stages or the compressor stages, wherein as described above liquid phases and vapour phases of the third refrigerant stream are separately compressed. Alternatively, all liquid phases are unified and pumped together.

[0085] In certain embodiments, the intermediate pressure is in the range of 10 bar(a) and 30 bar(a).

[0086] In certain embodiments, the third refrigerant stream is additionally separated into a mainly gaseous phase and a mainly liquid phase, wherein the mainly gaseous phase and the mainly liquid phase are separately expanded, particularly at different temperature levels, and separately guided with the feed gas stream, particularly in separate heat exchangers or in separate heat exchanger blocks. In certain embodiments, the mainly gaseous phase and/or the mainly liquid phase are expanded in a throttle valve.

[0087] In certain embodiments, the cooled feed gas stream is expanded in a sixth expansion device, thereby cooled. In certain embodiments, the fifth expansion device is a turbo-expander or a throttle valve. In certain embodiments, the fifth expansion device is a combination of a turbo-expander and a throttle valve.

[0088] In certain embodiments, at least one or all of above mentioned expansion devices comprise, particularly of the first, second, third and fifth expansion device, comprises at least one turbo-expander, wherein particularly the at least one turbo-expander is capable or designed to generate mechanical or electrical energy upon expansion of said respective streams, e.g. by means of a brake wheel, wherein particularly the at least one turbo-expander drives a compressor that partially or fully compresses the expanded first refrigerant stream and/or a compressor that compresses the expanded second refrigerant stream and/or a compressor that compresses the third refrigerant stream. The generated electrical energy may be supplied to the power grid or may be used elsewhere. Likewise, the generated mechanical energy may be used to compress any other as the above-mentioned streams.

[0089] In certain embodiments, the feed gas stream is pre-cooled from the initial temperature to a temperature in the range of 278K to 313K in a second precooling step. In certain embodiments, the second precooling step is performed by means of water cooling. In certain embodiments, at least one or all of the above-mentioned feed gas stream, first refrigerant stream, second refrigerant stream and third refrigerant stream are additionally pre-cooled before the precooling step by chilled water or cold devices using refrigerants as propane, propylene or carbon dioxide, particularly to temperature in the range of 230 K to 278 K.

[0090] In certain embodiments, the feed gas stream is provided with a pressure in the range of 15 bar(a) to 75 bar(a). In certain embodiments, the feed gas stream is provided with a pressure in the range of 25 bar(a) to 50 bar(a).

[0091] In certain embodiments, the feed gas stream is provided by compressing a feed gas stream comprising hydrogen at ambient temperature to a pressure of at least 15 bar(a), particularly in the range of 15 bar(a) to 75 bar(a), more particular in the range of 25 bar(a) to 60 bar(a), with at least one compressor, wherein particularly the compressor is a reciprocating piston compressor with at least one compressor stage, or an ionic liquid piston compressor.

[0092] In certain embodiments, the pre-cooled stream is further compressed by cold compression, particularly up to 90 bar, more particular up to 75 bar, even more particular to a pressure in the range of 25 bar(a) to 60 bar(a).

[0093] In certain embodiments, any one of all of the above-mentioned heat exchangers are plate-fin heat exchangers, particularly aluminium-brazed plate-fin heat exchangers. In certain embodiments, the precooling heat exchanger is a coil-wound heat exchanger.

[0094] In the following further features and advantages of the present invention as well as preferred embodiments are described with reference to the Figures, wherein

Fig. 1 shows a schematical illustration of a method according to the invention;

Fig. 2 shows a schema of an alternative of the method of the invention;

5 Fig.3 shows a schema of a further alternative of the method of the invention;

Fig.4 shows a schema of another alternative of the method of the invention.

Examples:

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[0095] The herein presented invention consists of a novel process design for hydrogen liquefaction on a large-scale, combining several process features to a new technically feasible and thermodynamically efficient configuration.

[0096] Particularly, the novel process includes the design of three efficient closed-loop refrigeration cycles providing cooling duty at different temperature levels between ambient temperature and liquid hydrogen temperature. This helps to match more closely the enthalpy-temperature curve within the plate-fin heat exchangers, significantly reducing refrigerant mass flow rates and energy consumption. Compared to aforementioned prior technologies with only one closed refrigeration cycle, the new invention can reduce specific energy consumption by as much as 30%, thus enabling an economical production of liquid hydrogen on a large-scale for e.g. clean energy applications. Advantageously, the hydrogen feed stream can be directly cooled and liquefied to the state of saturated or even subcooled liquid, with a final para-hydrogen that can be catalytically converted in the coldest plate-fin heat exchanger to contents above 99.9 % para.

[0097] The hydrogen feed gas cooling and liquefaction as well as the closed-loop refrigeration cycles are installed in at least one cold-box, preferably in two separate cold-box vessels 78,79 or more, for large-scale liquefaction capacities. The precooling cold box 78 contains the process equipment for the hydrogen feed gas cooling and part of the single-mixed refrigerant cycle, namely the aluminium-brazed plate-fin heat exchanger 81 and the feed gas purification units 76,77 (adsorber vessels). The feed gas cooling from the lower precooling temperature to liquid hydrogen state is installed in the liquefier cold box 79.

[0098] The cooling duty is provided by a configuration that is new to hydrogen liquefaction: a double closed-loop cold refrigeration cycle consisting of a main new Neon Brayton cycle (Cold-Cycle 1) and a low-temperature Hydrogen Claude cycle (Cold-Cycle 2) or Helium Brayton cycle for the cold-end liquefaction.

[0099] Cold-cycle 1 and cold-cycle 2 designs are optimized in pressure level and respective cooling temperature range. This allows an appropriate shifting of the respective refrigerant cooling duty and total mass flow rate of the two cycles in order to obtain optimal compressor and expander frame-sizes, in terms of energy-efficiency and technical feasibility.

[0100] A preferred plant design and method of the invention is described in the following with reference to Fig. 1.

Hydrogen liquefaction:

[0101] A normal hydrogen (25% para) feed gas stream 11 from a hydrogen production plant is fed to the liquefaction plant 100 with a feed pressure above 15 bar(a), particularly 25 bar(a), and a feed temperature near ambient temperature, particularly 303 K. The feed stream 11 with a mass flow rate above 15 tpd, particularly 100 tpd, is cooled down between 278 K and 308 K, particularly 298 K, with cooling water 75 before entering the precooling cold box 78 through plate-fin heat exchanger 81. A valve can be used to fill the refrigerant inventory for the hydrogen Cold-Cycle 2 directly from the purified feed stream downstream of 76,77.

[0102] The hydrogen feed 11 is cooled in the heat exchanger 81 to the temperature T-PC, particularly 100 K, by the warming-up low pressure streams 42 of the single mixed-refrigerant cycle, the neon cold-cycle 1 cold stream 28 and the hydrogen cold-cycle 2 cold stream 32. At the outlet of the heat exchanger 81, residual impurities are removed from the hydrogen feed gas 12 to achieve a purity of $\geq 99.99\%$ in the adsorber vessels 76, 77 by physisorption. The precooled feed gas 12 enters the adsorber unit at the temperature T-PC, particularly 100 K, which is about 20 K higher than in prior known hydrogen liquefier applications. Advantageously, the catalytic ortho-para conversion at this temperature runs thermodynamically more favourable.

[0103] After the feed gas purification, the stream 12 is routed back to the exchanger 81 through the catalyst filled passages of the plate-fin heat exchanger 81, where hydrogen naturally occurring with a para content of 25% is catalytically converted to hydrogen with a para content of about 39% and cooled to the temperature T-PC while the exothermic heat of conversion is being removed by the warming up refrigerants stream 28, 32 and/or 42 in the heat exchanger 81.

[0104] The precooled hydrogen feed stream 12 then enters the liquefier cold-box 78 with T - PC e.g. 100 K (between 90 K and 120 K). The feed stream 12 is subsequently cooled and liquefied as well as being catalytically converted to higher hydrogen para-fractions in one plate-fin heat exchanger 82 to 90.

[0105] The hydrogen gas feed stream 11 from battery-limits can be further compressed e.g. from 25 bar(a) to higher pressures, e.g. 75 bar(a), to increase process efficiency and to reduce volumetric flows and equipment sizes by means

of a one or two stage reciprocating piston compressor at ambient temperature, a one stage reciprocating piston compressor with cold-suction temperatures after precooling in the heat exchanger 81 or an ionic liquid piston compressor.

[0106] Alternatively, an adiabatic ortho-para catalytic converter vessel may be used in the precooling cold box 78 to pre-convert normal-hydrogen (25%) para to a para-fraction near equilibrium in the feed gas stream 12 at the outlet of adsorber 76,77, before routing the feed gas stream 12 back to the heat exchanger 81.

Detailed description of the single mixed-refrigerant precooling cold cycle

[0107] The precooling duty is provided by a new designed highly efficient single mixed-refrigerant (MR) cycle. The new MR composition in this invention has been optimized for hydrogen precooling to temperatures between 90 K and 120 K, thus differentiating itself from warmer cooling temperature applications as in natural gas liquefaction. In this embodiment, the MR mixture precooling is carried out down to a temperature T-PC of about 100 K.

[0108] A low pressure mixed-refrigerant stream 42 is routed through suction drum 71 to avoid that entrained liquid droplets from the warmed-up refrigerant stream 41 arrive at the suction side of stage one 63a of compressor 63. The MR composition and the discharge pressure of the first compression stage, between 10 bar(a) and 25 bar(a), are optimized to produce an intercooled stream 43 with a relatively high liquid fraction. This reduces the mass-flow of refrigerant 43 that has to be compressed in stage two 63b of the compressor 63. Through a phase separator 72 the intercooled refrigerant stream 43 is separated into a first liquid mixed refrigerant stream 45 that is pumped to the high pressure (particularly in the range of 25 bar(a) to 60 bar(a)) and into a first vapour refrigerant stream 44, which is compressed to high pressure (particularly in the range of 25 bar(a) to 60 bar(a)) by the second stage 63b of compressor 63. Both the vapour 44 and the liquid stream 45 are mixed to a two-phase high pressure mixed-refrigerant stream 41 after compression 63. The first vapour stream 44 may be additionally separated into a second liquid phase and a second vapour phase, wherein preferably the first liquid phase 45 and the second liquid phase are unified, pumped together to high pressure and afterwards unified with the second vapour phase before entering the precooling cold box 78. Alternatively, the low pressure mixed refrigerant stream may be compressed by more than two stages. If compression and after-cooling results in the formation of a liquid phase, additionally phase separators may be arranged between the compressor stages.

[0109] The two-phase high pressure mixed-refrigerant stream 41 enters the precooling cold-box 78 passing through the heat exchanger 81, where it is pre-cooled to the lower precooling temperature of 100 K. A Joule-Thomson valve 59 expands the pre-cooled mixed-refrigerant stream 41 to an expanded mixed refrigerant stream 42 that is characterized by an optimized low pressure level, particularly between 2 bar(a) and 8 bar(a). The refrigerant mixture of the high pressure mixed refrigerant stream 41 is designed to cool down from the temperature T-PC by more than 2.5 K, e.g. from 96 K to 100 K, through the Joule-Thomson expansion. The mixture temperature decrease is designed to maintain a feasible temperature difference between warming up and cooling down streams in the heat exchanger 81 as well as to assure that no component freeze-out occurs in the refrigerant mixture.

[0110] Additionally, the two-phase high pressure mixed-refrigerant stream may be additionally separated into a vapour and a liquid phase, wherein the liquid phase may be additionally pumped to high pressure and unified with the vapour phase before entering the precooling cold box 78. Alternatively, the vapour stream of the above mentioned additional separation is guided through the heat exchanger 81 and an additional heat exchanger or through two separate blocks of heat exchanger 81 in the precooling cold box 78, expanded in a throttle valve and guided again through both exchangers or blocks, whereby the liquid stream of the additional separation is guided through the additional heat exchanger or block, expanded in a throttle valve and guided again through the additional exchanger or block.

[0111] The MR composition can be regulated and controlled by the make-up system to adapt to ambient conditions and changed process conditions. The mixed-refrigerant is compressed in a turbo-compressor with at least two stages and inter-stage water cooling to decrease power requirement.

[0112] Alternatively, in a very simplified configuration, the low pressure refrigerant stream can be compressed within an at least two-stage compression 63 with inter-stage cooling without liquid fraction after the first compression stage 63a. Advantageously, no liquid pumps and no phase separator are required.

[0113] Low temperature precooling is efficiently achieved with a refrigerant mixture optimized specifically for hydrogen liquefaction, wherein the refrigerant preferably contains only four refrigerant components to maintain a manageable plant makeup system. A preferred mixture composition for a precooling temperature in the range of 90 K to 100 K consists of 23 mol. % nitrogen, 29 mol. % methane, 24 mol. % ethane and 0.24 mol. % isobutane. Ethylene may replace the ethane component for precooling temperature above 100 K. For precooling temperatures between 90 K and 100 K, iso-butane may be replaced by 1-butene, isopentane, propane or propylene (due to lower melting points).

[0114] The mixture of the mixed-refrigerant may be adapted depending on the precooling temperatures. Accordingly, the mixture may contain nitrogen, methane, ethylene, and n-butane, isobutane, propane, propylene isopentane, isobutane and/or n-pentane for temperatures between 100 K and 120 K (or higher).

[0115] For precooling temperatures between 80 K and 100 K, the mixture may contain nitrogen, argon, neon, methane,

ethane, propane, propylene, 1-butene.

[0116] Also alternatively, the hydrogen feed stream 11 may be pre-cooled to temperatures above 120 K, wherein in this case the mixed-refrigerant preferably contains nitrogen, methane, ethylene, n-pentane

[0117] For slightly higher process efficiencies, a fifth or more refrigerant mixture components can be added to the refrigerant mixture: iso-butane, iso-pentane, 1-butane, argon, neon, propane or propylene for precooling temperatures between 90 K and 100 K, or n-butane, iso-butane, iso-pentane, propane, propylene or pentane for precooling temperature T-PC particularly above 100 K, and additionally n-pentane, for precooling temperatures above 110 K.

Detailed description of the main cooling main cooling cold cycle 1:

[0118] A high pressure neon stream 21 enters the precooling cold-box 78 and is pre-cooled by the warming up streams 28, 32, 42 in the heat exchanger 81 to the precooling temperature T-PC, particularly 100 K. The pre-cooled neon stream 21 is separated in at least two neon turbine-strings 22, 23 to generate cooling work by nearly isentropic expansions (polytropic) in at least four turbine-expanders (51, 52, 53, 54). In the example herein depicted, two separate turbine-strings (22 and 23) are shown. One or maximal two additional separate turbine-strings with respectively one turbine can be added to this configuration at a higher temperature level to match more closely the temperature-enthalpy curve of cooling down and warming up streams in the heat exchangers. All said turbo-expanders 51, 52, 53, 54 are designed to partially recover energy by the means of turbine brakes coupled with a turbo-generator to produce electricity or via at least one compressor stage of Neon compressor 61 (Neon compander) to increase the total plant energy-efficiency.

[0119] The main cooling (neon) cold cycle 1 is unique to hydrogen liquefaction as it is combined with the Single-Mixed Refrigerant Precooling Cycle at the precooling temperature T-PC. The HP neon stream is cooled down in the heat exchanger 82 further from T-PC by the warming streams of the Cold-cycle 1 and Cold-cycle 2, namely by the low pressure hydrogen stream 32 and the low pressure neon stream 28.

[0120] In detail, the high pressure neon stream 21 is separated in two fractions: one fraction 22 is routed to turbine string 1, where the stream 22 is expanded in turbo-expander 51 to a medium-pressure level MP2 (medium pressure first partial neon stream 24). The MP2 stream 24 provides cooling duty to the cooling the down streams 11, 21, 31 in heat exchanger 84 as it is partially re-warmed before being expanded again in turbo-expander 52 to the low pressure level (to low pressure first partial neon stream 25). In this way, cooling with turbine string 1 is generated at two different pressure (low pressure and medium pressure) and temperature levels.

[0121] The second high pressure fraction 23 is subsequently cooled in the heat exchanger(s) 83, 84, 85, and 86 to the temperature of the second turbine string before being expanded in the turbine expander 53 to an intermediate pressure level MP1 (medium pressure second partial stream 26). This stream 26 is then re-warmed providing cooling to the cooling down streams 21,31,12 in heat exchanger 88 before finally being expanded to low pressure level (to the low pressure second partial neon stream 27) in the turbine expander 54. This new process configuration is particularly beneficial for hydrogen feed cooling for two reasons: the specific isobaric heat capacity of the hydrogen feed stream possesses steep gradients or even a peak close to its critical temperature (around 33 K).

[0122] The low pressure second partial stream 27 provides cooling duty to the cooling down streams 23, 31 up to the temperature of turbine outlet 52, where it is mixed to the low pressure first partial neon stream 25. The mixed stream 28 is warmed up close to ambient temperature as suction stream 28 for neon compressor 61, which is particularly a multi-stage (min. 3) turbo-compressor with stage intercooling. The hot compressor discharge stream 21 is cooled by a water-after-cooler before entering the precooling cold-box 78. The outlet temperature and pressure of neon turbo-expander 54 are optimized in combination with the Hydrogen Cold-cycle 2. The temperature of stream 27 is the cold-end temperature T-CE. T-CE is limited to about 26 K at the outlet of turbine expander 54, to maintain a safe margin from the neon melting point. Optimal cold-end temperatures T-CE are set between 26 K and 33 K (e.g. 28 K.) in order to design the compressor with a beneficial suction pressure above 1 bar(a).

[0123] Alternatively, the fraction 22 is expanded only to a medium pressure level MP2 (medium pressure partially expanded first partial stream 24), and mixed to the expanded second partial stream 27 (Figs. 2 and 3).

[0124] According to another alternative, the second high pressure fraction 23 is directly expanded to low pressure level (low pressure second partial stream 27) (Figs. 2 and 4).

[0125] Additionally or alternatively, a third high pressure fraction is separated from the neon high pressure fraction 21 and routed to a third turbine string 23 after being further cooled down by the warming up streams 28,32 and expanded to an intermediate pressure. This intermediate pressure stream is then re-warmed slightly before being expanded again in a turbo-expander 52 to the medium pressure level. In this way, cooling with the third turbine string is generated at two different pressure (medium and intermediate pressure) and temperature levels.

[0126] This new process configuration is particularly beneficial for hydrogen feed cooling since: depending on the pressure, the specific isobaric heat capacity of the hydrogen feed stream possesses steep gradients in the region close to its critical temperature (particularly between 30 K and 50 K). Alternatively, the third turbine string can be designed analogous to first and second turbine strings as described above, with no intermediate warming-up after the first turbine,

or with a slight cooling down between the expanders.

[0127] The low pressure neon stream 28 may be alternatively compressed at low temperature e.g. 150 K particularly by means of a turbo-compressor Advantageously, thereby the volumetric flow of the neon stream and thus the required equipment size for compression can be reduced, as well as the number of required compression stages resulting in a reduced frame-size and reduced capital costs.

[0128] Additionally, the above mentioned medium pressure partial neon stream 24 and 26 may be cooled or warmed in the heat exchangers 84 and 88, respectively. Alternatively, the above mentioned partial stream may be directly guided into the respective turbine expanders 52 and 54, without passing any heat exchanger.

Final cooling cold cycle 2:

[0129] Hydrogen is used as a refrigerant; in particular normal hydrogen with an approximate 25% para-fraction is used as a preferred refrigerant. The high pressure hydrogen refrigerant 31 is precooled in the heat exchanger 81 (stream 31) to T-PC, particularly 100 K. In the liquefier cold-box 79, the high pressure hydrogen refrigerant 31 is then subsequently cooled down to a temperature around 28 K. At the cold end, the hydrogen cold-cycle provides the cooling for the final liquefaction and final ortho-para conversion and subcooling of the hydrogen feed stream 13, 14. The high pressure hydrogen refrigerant 31 is expanded from high pressure to low pressure in at least one turbine string though at least one turbo-expander 55, wherein particularly a second turbine string with an additional turbo-expander or more turbine strings may be added. If this turbo-expander 55 is to be designed with a dry-gas discharge, the high pressure hydrogen refrigerant 31 is expanded from high pressure to an intermediate pressure, above the critical pressure or to a pressure in the range of 5 bar(a) to 13 bar(a) if no two-phase is generated within the turbine 57 or at the outlet of the turbine 57. Subsequently, the cooled stream is expanded to low pressure 32 through a Joule-Thomson throttle valve 56 into a gas-liquid separator 74. For a turbo-expander with allowed two-phase discharge, e.g. a wet expander, the high pressure hydrogen refrigerant 31 can be expanded directly to low pressure level 32. Alternatively, a cold liquid piston expander can be employed to expand the high pressure stream 31 directly to low pressure level 32 into the two-phase region. In either case, the low pressure level 32 is fixed to provide a cooling temperature below the feed temperature for saturated or even subcooled liquid (between 20 K and 24 K).

[0130] The low pressure hydrogen refrigerant 32 is warmed-up to near ambient temperature providing cooling duty to the cooling down streams in the precooling 78 and liquefier cold-box 79. The warmed low pressure hydrogen refrigerant 32 is compressed in one multi-stage reciprocating piston compressor 62 with inter-stage cooling. The piston compressor 62 is designed with at least three intercooled stages. Alternatively, the low pressure hydrogen refrigerant 32 may be compressed in an ionic liquid piston compressor. As a further alternative, the low pressure hydrogen refrigerant is warmed up to a temperature below the ambient temperature e.g. to 150 K in the precooling heat exchanger 81 before compression.

[0131] Alternatively, the high pressure refrigerant 31 is separated into at least two partial streams, wherein the first partial stream is expanded to low pressure level as described above, and the second partial stream is expanded in an additional turbo-expander to a medium pressure level (between high and low pressure) and guided into the expanded first partial stream between two compressor stages, in which the expanded first partial stream is compressed from low pressure level to high pressure level, particularly after a compressor stage, in which the expanded first partial stream is compressed to a pressure level close to the medium pressure level of the partially expanded second partial stream. Such configuration is particularly advantageously, if the first temperature T-CE, provided by the main cooling cycle, is above 32 K.

[0132] After cooling the hydrogen feed stream 13 to a temperature equal to the cooled high pressure hydrogen refrigerant 31, e.g. 28 K, the feed stream is catalytically converted to a para-fraction slightly below the equilibrium para-fraction at T-CE or as required. The stream 13 is then expanded by the means of at least one turbo-expander from feed pressure to an intermediate pressure above the critical pressure or to a pressure in the range of 5 bar(a) to 13 bar(a) if no two-phase is generated within the turbine 57 or at the outlet of the turbine 57. Subsequently, the expanded and cooled feed stream 14 is further expanded through the Joule-Thomson throttle valve 58 to the low pressure level near the final product storage pressure e.g. 2 bar(a).

[0133] For turbo-expanders allowing a two-phase discharge, the cooled hydrogen feed stream 13 can be directly expanded into the two-phase region to the final product storage pressure e.g. 2 bar(a). For shaft powers around 50 kW or higher, as in large-scale liquefiers with e.g. 100 tpd capacity, a turbo-expander with energy-recovery via a turbo-generator can be employed to raise energy-efficiency. Alternatively, a cold liquid piston expander can be employed to directly expand the feed stream from the intermediate pressure level, e.g. 13 bara, to the low pressure level near the final product storage pressure. In either case, the two-phase hydrogen feed stream 14 is finally cooled and catalytically converted in the last part of the plate-fin heat exchanger 91 against the warming up Cold-cycle 2 refrigerant stream 32.

[0134] Alternatively, a high pressure Helium Brayton cycle is employed as a separate closed-loop refrigerant cycle, instead of the above described hydrogen cold cycle 2, to provide the cooling duty at temperatures below the cold-end T-CE. In this case, compressor 62 is a helium compressor. The high pressure helium stream is expanded and is routed

back to the cold-box 79 in a separate closed-loop cycle. The high pressure helium Brayton refrigeration cycle is capable of providing refrigeration at temperatures significantly below the normal boiling point of the hydrogen feed, due to the low melting point of helium. Helium is expanded in a turbo-expander from high pressure in range of 50 bar(a) to 70 bar(a) to low pressure in the range of 5 bar(a) to 25 bar(a) to provide cooling duty for the cooling and liquefaction of the hydrogen feed stream. The helium compression from low pressure to high pressure at near ambient temperature can be implemented through highly-efficient new ionic liquid piston compressor technology (Linde Ionic Compressor). This feature is new to the hydrogen liquefaction process.

[0135] With this configuration, a liquid hydrogen product stream 15 at the outlet can be generated as saturated liquid or even subcooled liquid, a final para-fraction of F-LH2-01 above 99.5% can be reached, depending on temperature of the liquid hydrogen product.

[0136] The method of the invention offers the following advantages:

In summary:

- Significant decrease in specific energy demand and specific costs for the production of liquid hydrogen on a large-scale compared to prior known technologies
- New process configuration combining a highly efficient Single-Mixed Refrigerant precooling cycle (precooling cold box) with a Neon Brayton and Hydrogen Claude-Cycle (liquefier coldbox) for large-scale hydrogen liquefaction
- New refrigerant mixture for hydrogen liquefaction enabling precooling temperatures T-PC between 90 K and 120 K e.g. 100 K, which are significantly lower than in conventional mixed-refrigerant technology applications e.g. for natural gas liquefaction. Temperature decrease from T-PC across Joule-Thomson expansion valve is designed to maintain safety margin to the mixture melting point to avoid component freeze out
- The low precooling temperature for the mixed-refrigerant combines the benefits of a high energy-efficient single mixed-refrigerant cycle with comparatively low precooling temperatures. This is beneficial because of the decreased cooling duty to be provided by the cold-cycle, thus reducing equipment size in the colder refrigeration cycle, e.g. size of heat exchanger, compressor and turbine
- Double closed-loop cold-cycle configuration providing cooling at different temperature levels:
 - Combination of the advantages of both neon and normal-hydrogen as refrigerants: feasible turbo-compressor stage pressure ratios at ambient temperature (neon) and low melting point of hydrogen.
 - For the pressure ratios and volumetric gas flows required by conventional refrigeration cycles for large-scale hydrogen liquefaction, turbo-compressors for ambient temperature suction for 100 mol. % helium and 100 mol. % hydrogen refrigerant would require complex designs with impracticable high number of compression stages per machine or very high wheel tip speeds and thus rotational speeds which are currently difficult to implement.
 - Screw compressors for helium or hydrogen have a low isentropic efficiency. Reciprocating compressor are limited in frame-size principally by the maximum practicable volumetric suction flow rates. Prior known designs for hydrogen reciprocating compressors for large-scale hydrogen liquefiers with e.g. up to 150 liquefaction capacity, would require three or more very large reciprocating piston compressors with among the largest available frame-sizes, and thus footprint, to operate in parallel. This would be an unfavourable design in terms of investment costs, plant maintainability, reliability and availability. Industrial gas plants with reciprocating compressors that require favourable turndown capabilities as well as economically feasible investment and operating costs (plant availability), are typically designed with reciprocating compressors in a 2 x 100% configuration.
 - Neon Cold-cycle 1 requires only one multi-stage turbo-compressor machine for large-scale liquefaction capacities of up to 150 tpd. The total rotating equipment count of the hydrogen liquefaction plant is reduced compared to known technologies.
 - Compared to helium and hydrogen, the neon fluid properties allow the design of highly efficient turbo-expanders with energy recovery and moderate (technically viable) rotational speeds for the high cooling duty cold-cycle. The presented neon expander process configuration with two turbine strings provide cooling duty at three different pressure levels (MP1, MP2, LP) with the means of available cryogenic turbo-expander frame sizes (wheel diameters) and comparatively high isentropic efficiencies.
 - Hydrogen Cold-cycle 2 is a small refrigeration cycle at the cold-end in large-scale liquefiers: the resulting moderate hydrogen refrigerant volumetric flow enables the use of only one reciprocating piston compressor machine (also at high hydrogen liquefaction capacities) or, alternatively, an ionic liquid piston compressor. This design avoids the use of two or more large piston compressors running in parallel (higher maintenance I downtimes).

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- Hydrogen Cold-cycle 2: because of the low melting point of hydrogen (14 K), the closed-loop cycle can provide the cooling duty for the coldest part of the liquefier. The hydrogen cycle effectively cools down the feed hydrogen to produce directly saturated or even subcooled liquid e.g. 2 bara, 22.8 K. Compared to prior known technologies employing only neon as cold-cycle refrigerant, product para-fractions above 99.5% can be reached.
 - Helium Cold-Cycle 2: as an alternative, a compact helium Brayton cycle can be implemented with this configuration. Machine equipment related to helium is economically less expensive. The low helium boiling point allows for the use of a high pressure Brayton cycle with reduced volumetric flows to reach very low cooling temperatures (> 14 K) for the hydrogen feed.
 - The separation of the colder refrigeration cycle in two closed-loop cycles (Neon and Hydrogen cycles) increases the flexibility of the liquefaction plant.
 - The cold-cycle compression in Cold-Cycle 1 and/or Cold-Cycle 2 can be performed at cryogenic suction temperatures (cold compression) alternatively to the state-of-the-art warm suction compression. This configuration would further reduce compressor frame sizes and number of required stages for compressor 61 and/or 62.
- Feed I Cold-cycle 2 compression: the presented new process configuration enables the application of innovative ionic compression technology in a hydrogen liquefaction process, with significantly higher isentropic efficiencies compared to conventional compressor technology (new to hydrogen liquefaction)
 - Start of the continuous catalytic ortho-para conversion in plate-fin heat exchanger directly after the mixed-refrigerant precooling is set at a temperature level, e.g. 100 K, which is significantly higher than in conventional liquefiers.. Due to the removal of exothermic heat of conversion at a higher temperature level, the thermodynamic efficiency of the plant is improved. This can be realized by installing an adsorption unit at e.g. 100 K. The adsorption vessel (physisorption) removes residual impurities from the hydrogen feed which can poison the catalyst.

Reference Numerals

100	hydrogen liquefaction plant
11	hydrogen feed stream (25 bar(a), ambient temperature)
12	precooled hydrogen feed stream (100 K, 25 bar(a))
13	cooled hydrogen feed stream (27 K to 35 K)
14	expanded cooled hydrogen feed stream (2 bar(a))
15	Liquid hydrogen product stream
21	high pressure neon stream (bara)
22	high pressure first partial neon stream (bara)
23	second high pressure partial neon stream (bar(a))
24	medium pressure first partial neon stream (bar(a))
25	low pressure first partial stream (bar(a))
26	medium pressure second partial neon stream (bar(a))
27	low pressure second partial neon stream (bar(a))
28	low pressure neon stream (unified, bar(a))
31	high pressure hydrogen stream
32	low pressure hydrogen stream
33	vapour phase of low pressure hydrogen stream

(continued)

34	liquid phase of low pressure hydrogen stream
41	high pressure mixed refrigerant stream
42	low pressure mixed refrigerant stream
43	medium pressure mixed refrigerant stream
44	vapour phase of medium pressure mixed refrigerant stream
45	liquid phase of medium pressure mixed refrigerant stream
51,52,53,54,55,57	turbo-expander
56,58,59	throttle valve
61	turbo compressor
62	piston compressor
63a	first compressor stage
63b	second compressor stage
64,65	pump
71	suction drum
72,73,74	phase separator
75	water cooling
76,77	adsorber vessel
78	pre cooling cold box
79	liquefier cold box
81,82,83,84,85,86,87,88,89, 90,91	heat exchanger block or heat exchanger filled with ortho-para catalyst (hatched area)

Claims

1. Method for liquefying hydrogen, the method comprises the steps of:

- providing a feed gas stream (11) comprising hydrogen, wherein said feed gas stream (11) is **characterized by** an initial temperature and a pressure of at least 15 bar(a),
- precooling said feed gas stream (11) from said initial temperature to an intermediate temperature in a precooling step yielding a precooled feed gas stream (12), wherein particularly said intermediate temperature is in the range of 70 K to 150 K,
- cooling said precooled feed gas stream (12) to a temperature below the critical temperature of hydrogen yielding a liquid product stream (15) comprising hydrogen,

characterized in that

- said precooled feed gas stream (12) is cooled to a first temperature in a first cooling step by a first closed cooling cycle with a first refrigerant stream (21) consisting of or comprising neon and/or hydrogen, wherein said first refrigerant stream (21) is expanded, thereby producing cold, and
- said cooled feed gas stream (13) is further cooled from said first temperature to a temperature below the critical temperature of hydrogen, particularly below 24 K, in a second cooling step by a second closed cooling cycle

with a second refrigerant stream (31) comprising or consisting of hydrogen and/or helium, wherein said second refrigerant stream (31) is expanded, thereby producing cold.

2. The method according to claim 1, **characterized in that** said feed gas stream (11) is precooled in said precooling step by a closed precooling cycle with a third refrigerant stream (41), wherein said third refrigerant stream (41) is expanded, thereby producing cold, and said third refrigerant stream (41) comprises or consists of nitrogen, a mixture of C₁-C₅ hydrocarbons or a mixture of nitrogen and C₁-C₅ hydrocarbons.
3. The method according to claim 2, **characterized in that** said third refrigerant stream (41) comprises or consists of four components, wherein a first component is nitrogen, a second component is methane, a third component is ethane or ethylene, and a fourth component is n-butane, isobutane, propane, propylene, n-pentane or isopentane.
4. The method according to one of the preceding claims, **characterized in that** said feed gas stream (11) is precooled in said precooling step to an intermediate temperature equal or above 80 K, particularly in the range of 85 K to 120 K yielding said precooled feed stream (12), and said precooled feed stream (12) is brought into contact with a catalyst being able to catalyse the conversion of ortho hydrogen to para hydrogen.
5. The method according to one of the preceding claims, **characterized in that** said first cooling cycle comprises the steps of:
 - providing said first refrigerant stream (21) with a first pressure,
 - separating said first refrigerant stream (21) at least into a first partial stream (22) and a second partial stream (23),
 - expanding said first partial stream (22) in a first expansion device (51, 52) to a first intermediate pressure yielding an partially expanded first partial stream (24) and/or to a second pressure yielding an expanded first partial stream (25),
 - expanding said second partial stream (23) to a third pressure in a second expansion device (53, 54) yielding an expanded second partial stream (27),
 - guiding said expanded second partial stream (27) and said precooled feed gas stream (12) such that heat can indirectly be transferred between said expanded second partial stream (27) and said precooled feed gas stream (12), thereby particularly cooling the precooled feed gas stream (12) to the first temperature,
 - merging said partially expanded first partial stream (24) or said expanded first partial stream (25) with said expanded second partial stream (27) yielding an expanded first refrigerant stream (28), and
 - compressing said expanded first refrigerant stream (28) to the first pressure yielding said first refrigerant stream (21).
6. The method according to claim 5, **characterized in that** said first partial stream (22) is expanded to a first intermediate pressure yielding said partially expanded first partial stream (24), said partially expanded first partial stream (24) and said second partial stream (27) are guided such that heat can indirectly be transferred between said partially expanded first partial stream (24) and said second partial stream (27), thereby particularly cooling said second partial stream (27), and said partially expanded first partial stream (24) is further expanded to said second pressure yielding said expanded first partial stream (25).
7. The method according to claim 5 or 6, **characterized in that** said second partial stream (23) is expanded to a second intermediate pressure yielding a partially expanded second partial stream (26), said partially expanded second partial stream (26) and said precooled feed gas stream (12) and/or said second refrigerant stream (31) are guided such that heat can indirectly be transferred between said partially expanded second partial stream (26) and said precooled feed gas stream (12) and/or said second refrigerant stream (31).
8. The method according to one of the preceding claims, **characterized in that** said second cooling step comprises the steps of:
 - providing said second refrigerant stream (31) with a fourth pressure,
 - expanding said second refrigerant stream (31) in a third expansion device (55, 56) to a fifth pressure yielding an expanded second refrigerant stream (32),
 - guiding said expanded second refrigerant stream (32) and said cooled feed gas stream (13) such that heat can indirectly be transferred between said expanded second refrigerant stream (32) and said cooled feed gas stream (13), thereby liquefying said cooled feed gas stream (13) to said liquid product stream (15),
 - compressing said expanded second refrigerant stream (32) to said fourth pressure yielding said second re-

frigerant stream (31).

9. The method according to one of the preceding claims, **characterized in that** said precooling step comprises the steps of:

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- providing said third refrigerant (41) with a sixth pressure,
- expanding said third refrigerant stream (41) in a fourth expansion device (59) to a seventh pressure yielding an expanded third refrigerant stream (42),
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- guiding said expanded third refrigerant stream (42) and said feed gas stream (11) such that heat can indirectly be transferred between said expanded third refrigerant stream (42) and said feed gas stream (11), thereby particularly precooling said feed gas stream (11) to said intermediate temperature,
- compressing said expanded third refrigerant (42) to said sixth pressure in a first precooling compressor yielding said third refrigerant (41).

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10. The method according to claim 9, **characterized in that** compressing said expanded third refrigerant stream (42) comprises the steps of:

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- compressing said expanded third refrigerant stream (42) in said first precooling compressor (63) or a first compressor stage (63a) of said first precooling compressor (63) to an intermediate pressure yielding an intercooled third refrigerant stream (43),
- separating said intercooled third refrigerant stream (43) into a mainly liquid third refrigerant stream (45) and a mainly gaseous third refrigerant stream (44), wherein said mainly liquid third refrigerant stream (45) is pumped to said sixth pressure, and said mainly gaseous third refrigerant stream (44) is compressed in a second precooling compressor or a second compressor stage (63b) of said first precooling compressor (63) to said sixth pressure,
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- combining said compressed mainly liquid third refrigerant (45) and said compressed mainly gaseous third refrigerant (44) to said third refrigerant stream (41).

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11. The method according to claim 10, **characterized in that** said third refrigerant stream (41) is additionally separated into a mainly gaseous phase and a mainly liquid phase, wherein said mainly gaseous phase and said mainly liquid phase are separately expanded, and said expanded phases and said feed gas stream (11) are guided such that heat can indirectly be transferred between said expanded phases and said feed gas stream (11).

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12. The method according to one of the preceding claims, **characterized in that** said cooled feed gas stream (13) is expanded in a fifth expansion device (57, 58) to a storage pressure and thereby further cooled, particularly within said second cooling step, wherein particularly the storage pressure is in the range of 1 bar(a) to 3.5 bar(a), more particular in the range of 1.8 bar(a) to 2.5 bar(a).

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13. The method according to one of claims 5 to 12, **characterized in that** at least one or all of said first (51, 52), second (53, 54), third (55) and fifth expansion device (57) comprises at least one turbo-expander.

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14. The method according to claim 13, **characterized in that** said at least one turbo-expander (51, 52, 53, 54, 55, 57) is designed to generate mechanical or electrical energy upon expansions of the respective stream (22, 23, 24, 26, 31).

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15. The method according to one of the preceding claims, **characterized in that** said precooled feed gas stream (12) is further compressed to a pressure above 15 bar(a), particularly up to 90 bar(a), more particularly up to 75 bar(a), even more particular between 25 bar(a) and 60 bar(a).
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Fig. 1

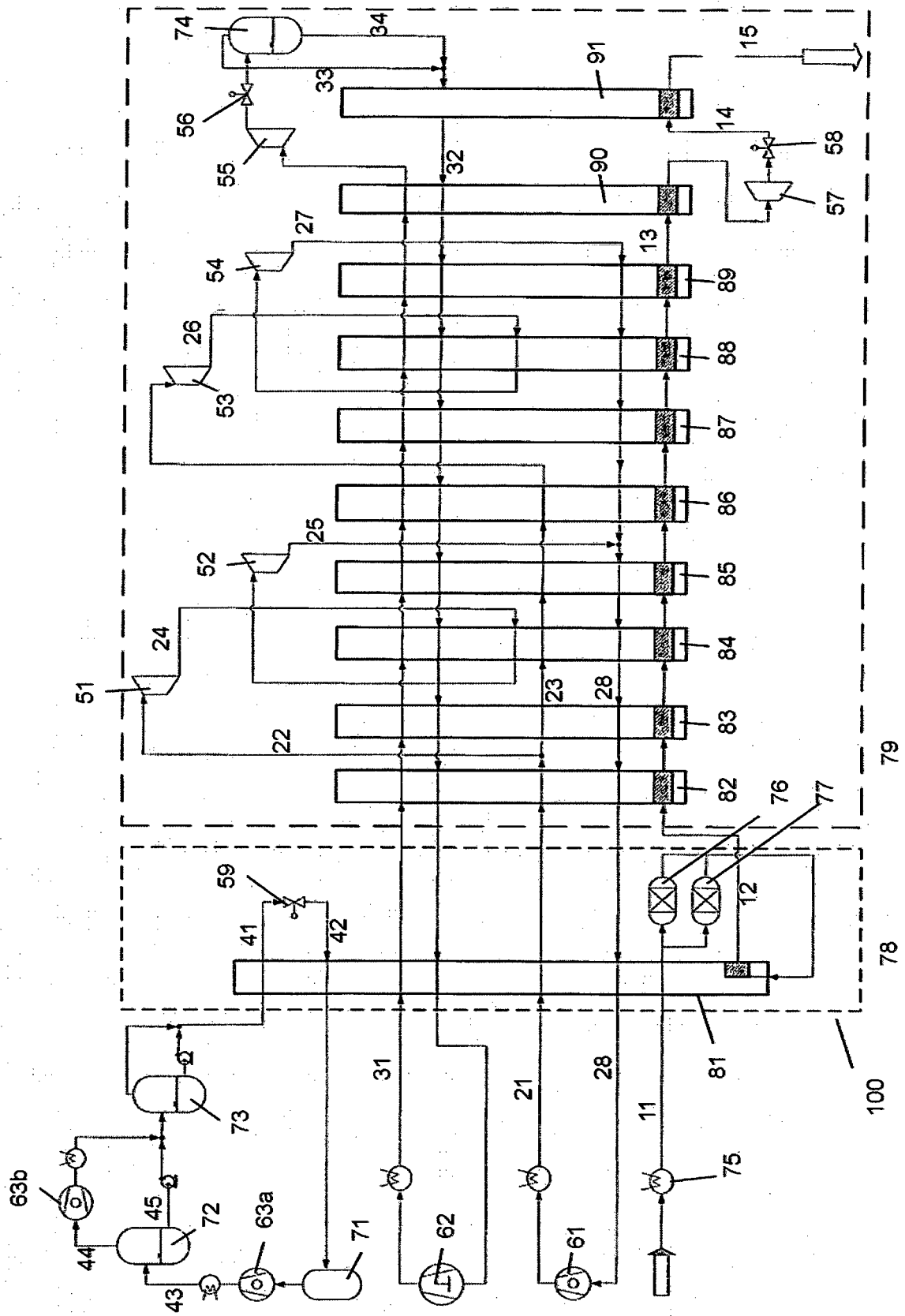


Fig. 2

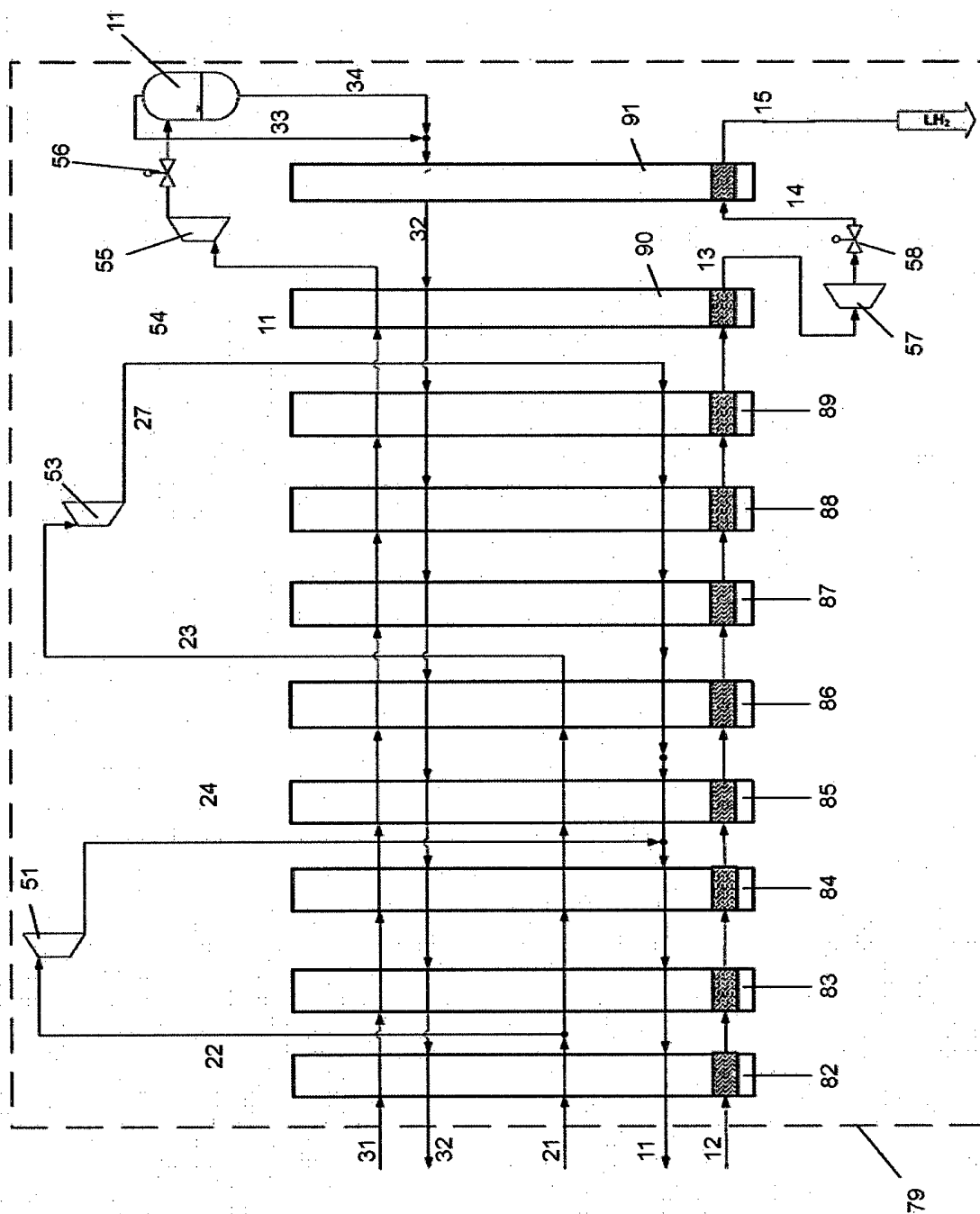


Fig. 3

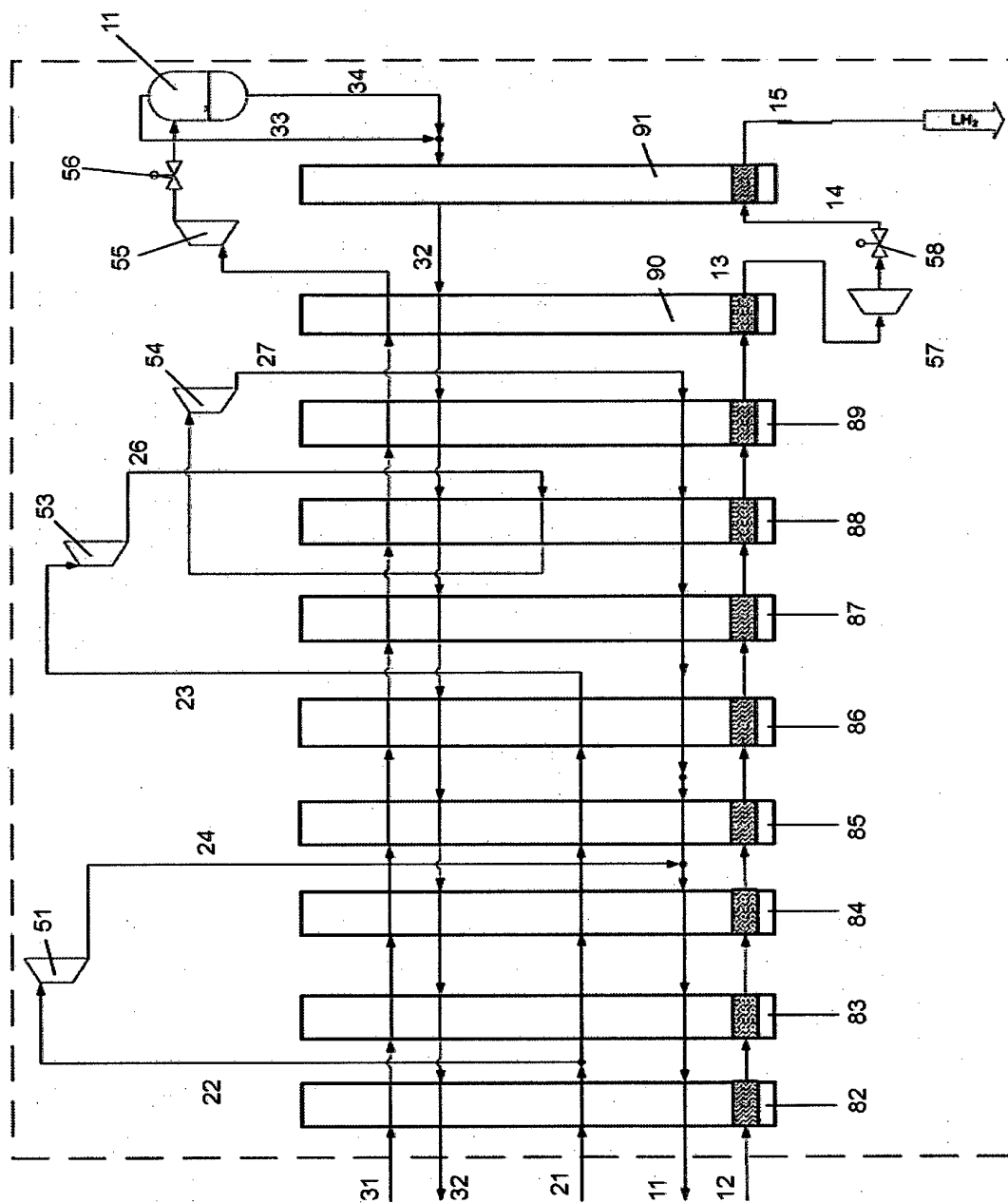
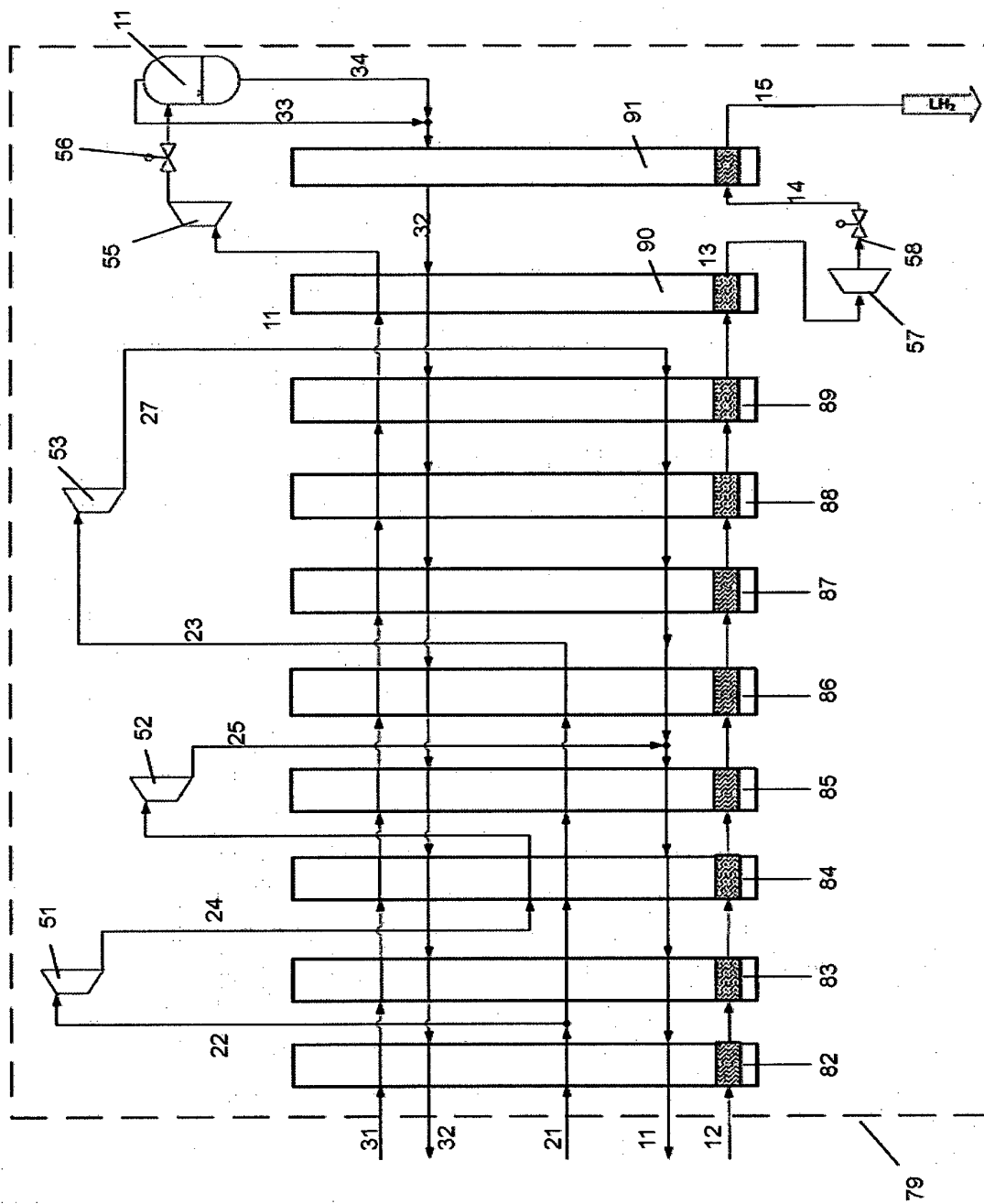


Fig. 4





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Place of search Munich		Date of completion of the search 27 April 2016	Examiner Göritz, Dirk
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Place of search		Date of completion of the search	Examiner
Munich		27 April 2016	Göritz, Dirk
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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