

Description

Title of the invention: Method and plant for hydrogen liquefaction

Technical field

5 [0001] The present disclosure concerns the field of cryogenics, and more specifically that of hydrogen liquefaction.

Prior art

10 [0002] In order to limit greenhouse gas emissions, hydrogen, preferably obtained using non-carbon energy sources, is being considered more and more as an energy carrier. However, in order to obtain an energy density which allows it to rival hydrocarbons, in particular for transport applications, it is generally preferred to transport and store it in liquid form.

15 [0003] However, hydrogen liquefaction requires considerable energy consumption. Thus, the specific energy consumption of hydrogen liquefaction plants currently in service is approximately 12 at 15 kWh per kilogram of liquefied hydrogen. For example, the company Linde®, on its site at Leuna, operates a liquefaction plant applying the Claude cycle to hydrogen, combined with a precooling using the evaporation of liquid nitrogen, as described by Berstad, Stang and Neksa in
20 "Comparison criteria for large-scale hydrogen liquefaction processes", International Journal of Hydrogen Energy, vol. 34, no. 3, February 2009, pages 1560-1568. This plant has a specific energy consumption of 11.9 kWh per kilogram of liquefied hydrogen.

25 [0004] Several alternatives have been proposed in order to reduce the cost and energy consumption of hydrogen liquefaction. Thus, in "Large scale hydrogen liquefaction in combination with LNG re-gasification", Proceedings of the 16th World Hydrogen Energy Conference 2006, pages 3326–3333, Kuendig, Lorchlein, Kramer and Huijsmans proposed replacing, as the cold source, the evaporation of liquid nitrogen by that of liquefied natural gas, thus obtaining a synergy with the
30 processes requiring natural gas in the gaseous state. Other authors have proposed alternatives to the Claude cycle with hydrogen. Thus, Matsuda and

Nagami have proposed, in "Study of large hydrogen liquefaction process", Hydrogen Energy, 1997, page 175, applying the Brayton cycle with helium, or even with neon as refrigerant. The Brayton cycle with helium was also proposed by Kuz'menko, Morkovkin and Gurov in "Concept of building medium-capacity hydrogen liquefiers with helium refrigeration cycle", Chemical and Petroleum Engineering, 2004, 40(1/2), pages 94–98. However, the Brayton cycle with helium does not lend itself well to large-scale exploitation. For this reason, Valenti and Macchi have proposed, in "Proposal of an innovative, high-efficiency, large-scale hydrogen liquefier", International Journal of Hydrogen Energy, 2008, 33(12), pages 3116–3121, a method applying four Joule-Brayton cycles in cascade. In practice, the energy efficiency of this method does not however appear to be guaranteed.

[0005] Quack, in "Conceptual design of a high efficiency large capacity hydrogen liquefier", AIP Conference Proceedings, 2002, 613, pages 255–263, proposed a method comprising an initial compression of hydrogen, followed by a precooling with propane, a cooling applying a two-stage reverse Brayton cycle with "nelium" (a mixture of helium and neon in molar proportions 4: 1), and expansion in a rotary gas expansion valve. Within the framework of the European project IdealHY, a method for liquefying hydrogen was conceived comprising a precooling with mixed refrigerant (MR, designating a mixture comprising nitrogen and hydrocarbons), followed by cooling with "nelium" and liquefaction by expansion, while Krasae-in has described, in "Optimal operation of a large-scale liquid hydrogen plant utilizing mixed fluid refrigeration system", International Journal of Hydrogen Energy, 2014, 39(13), pages 7015–7029, a method for hydrogen liquefaction comprising a precooling with MR and cooling applying a cascade of Joule-Brayton cycles with hydrogen, and theoretically making it possible to obtain a specific energy consumption of just 5.35 kWh per kilogram of liquefied hydrogen for a large-scale production of 100 metric tonnes per day.

[0006] The specification of European patent application EP 1 580 506 A1 disclosed a method and a plant for hydrogen liquefaction with a precooling step by liquefied natural gas and a cooling step by a refrigerant compressed at low-temperature in compressors also cooled by liquefied natural gas, while Howe, Skinner and Finn disclosed, in "Advanced precooling for optimized hydrogen liquefaction", H2Tech,

March 2021, other methods and plant for hydrogen liquefaction with a precooling step by a first refrigerant and a cooling step by a second refrigerant. Finally, other methods and plants for hydrogen liquefaction have been disclosed in the publications of Japanese patent applications JP 2004-210597 A and JP S61-140777.

Disclosure of the invention

[0007] A first aspect of the disclosure relates to a method for hydrogen liquefaction providing a reduced specific energy consumption through greater efficiency of a refrigerant compression step, and this with an adjustable flow of liquid hydrogen.

[0008] For this, in the method according to this first aspect, which comprises a pre-cooling step, wherein a hydrogen feed flow is cooled by a first refrigerant, a cooling step, wherein the hydrogen feed flow is cooled by a second refrigerant, and a step of expanding the hydrogen feed flow, each of the first and second refrigerants is successively subjected to at least one compression and to at least one expansion in order to cool it, and a liquid phase of the first refrigerant cools the second refrigerant between at least three stages of a compression of the second refrigerant, so that the second refrigerant does not exceed a temperature of 150 K, preferably 113 K, during said compression of the second refrigerant.

[0009] The expansion of the hydrogen feed flow can, in particular, be a substantially adiabatic expansion. The term "substantially adiabatic" shall mean, in the context of the present disclosure, an expansion in which the enthalpy does not vary substantially, for example does not vary by more than 5%, or even 1%, insofar as this can be obtained by conventional means such as, in particular, Joule-Thomson effect valves, thermally insulated expansion valves.

[0010] Through division of the compression of the second refrigerant between at least three successive stages, and through the use of the first refrigerant for cooling the second refrigerant between at least three stages of this compression, it is thus possible to maintain the temperature of the second refrigerant below the threshold of 150 K, or even 113 K, in order to thus attain a high degree of energy efficiency in the cooling step of the hydrogen feed flow by the second refrigerant.

[0011] The first refrigerant can, in particular, comprise nitrogen and/or argon.

Through the choice of nitrogen and/or argon as first refrigerant, it is therefore possible to carry out said compression of the second refrigerant at a particularly low temperature, which allows the energy efficiency of the cycle of the second refrigerant to be increased.

[0012] The liquid phase of the first refrigerant can cool the second refrigerant upstream of each of said at least three compression stages of the second refrigerant, in such a way that the initial temperature of the second refrigerant in each of said at least three stages is substantially identical, thus facilitating the use of common elements for said at least three compression stages.

[0013] The second refrigerant can comprise mainly, or even uniquely, hydrogen.

Alternatively and in addition to hydrogen, the second refrigerant can nevertheless comprise neon and/or helium, in order to increase the density and thus to optionally enable its compression in fewer stages.

[0014] In order to allow a gradual cooling of the hydrogen feed flow over a large range of temperatures, the second refrigerant can be divided into a first stream which is subject to an expansion for cooling and a second stream which is cooled by the first stream of the second refrigerant after the expansion of the first stream of the second refrigerant. The second stream of the second refrigerant can be subject to an expansion, in particular to a substantially adiabatic expansion, after having been cooled by the first stream of the second refrigerant.

[0015] Analogously and for the same reasons, the first refrigerant can also be divided into a first stream which is subject to an expansion in order to cool it and a second stream which is cooled by the first stream of the first refrigerant after the expansion of the first stream of the first refrigerant. The first stream of the second refrigerant can also be subject to an expansion, in particular to a substantially adiabatic expansion, after having been cooled by the first stream of the second refrigerant.

[0016] In order to improve the efficiency of the precooling, the hydrogen feed flow can also be cooled by a third refrigerant during the precooling step.

[0017] A second aspect of the present disclosure relates to a plant for hydrogen liquefaction, which may be able to implement the method of the first aspect and

comprising, for this purpose, at least one hydrogen feed circuit, a first refrigerant circuit, in particular a closed loop circuit, containing a first refrigerant, a second refrigerant circuit, in particular a closed loop circuit, containing a second refrigerant, a first heat exchanger assembly passed through by the hydrogen feed circuit and by the first refrigerant circuit, a second heat exchanger assembly passed through by the second refrigerant circuit and by the hydrogen feed circuit downstream of the first heat exchanger assembly, and an expansion valve passed through by the hydrogen feed circuit downstream of the second heat exchanger assembly. In the present context, the term "expansion valve" shall mean any device capable of implementing an expansion of a fluid, whether this be with extraction of work, as for example in a turbine, or substantially adiabatically, as for example in an adiabatic expansion valve. The terms "upstream" and "downstream" should be understood as following in the normal direction of circulation of the fluid in each circuit.

[0018] In order to attain a high degree of energy efficiency in the cooling of a hydrogen feed flow, the first refrigerant circuit can comprise one or more compressors and one or more expansion valves, and the second refrigerant circuit can comprise at least three compressors and a cooling device disposed together so as to carry out at least three compressions of the second refrigerant without exceeding a temperature of 150 K, preferably 113 K, and one or more expansion valves. The cooling device can be configured for cooling the second refrigerant in the second refrigerant circuit with a liquid phase of the first refrigerant in the first refrigerant circuit, in particular in a tank of the first refrigerant circuit. In particular, the second refrigerant circuit comprises a plurality of intermediate exchangers interposed between said at least three compressors of the second refrigerant circuit, and optionally disposed in the tank of the first refrigerant circuit, in order to maintain the temperature of the second refrigerant. In order to obtain a substantially identical inlet temperature for each of said at least three compressors of the second refrigerant circuit, and thus to facilitate the use of substantially identical elements for each of said at least three compressors of the second refrigerant circuit, one of said intermediate exchangers can be disposed upstream of each of said at least three compressors of the second refrigerant circuit.

[0019] Lubricant is normally present in the bearings of volumetric compressors typically used in plants for hydrogen liquefaction and can escape into the refrigerant stream. However, at the cryogenic temperatures at which the compressors of the second refrigerant circuit operate, these lubricant leaks could have harmful effects in this second refrigerant circuit, and require a device for extracting this lubricant. In order to avoid this, said compressors of the second refrigerant circuit can have magnetic bearings, in particular active magnetic bearings. Furthermore, in order to reduce the wear that is frequently associated with volumetric compressors, these can be centrifugal compressors. They can also be electrically driven, so as to be compatible with their total or partial immersion in the liquid phase of the first refrigerant at cryogenic temperature.

[0020] In order to ensure isomeric stability of the hydrogen from the feed flow downstream of each heat exchanger, at least one heat exchanger of the first assembly or the second assembly can be a catalytic exchanger, exposing the feed flow to a catalyst such as, for example, trivalent iron oxide, in order to perform an ortho-para catalytic conversion.

[0021] In order to maintain the temperature of the first refrigerant during its compression, and thus to ensure a substantially isothermal compression, the compressors of the first refrigerant circuit can be water-cooled. However, air-cooling is also possible for the compressors of the first circuit.

[0022] In order to ensure gradual and energetically efficient cooling, the second refrigerant circuit can include a branching, downstream of said compressors of the second refrigerant circuit, with a first branch including one or more of said expansion valves of the second refrigerant circuit upstream of at least one of the heat exchangers of the second assembly downstream, and a second branch passing through at least one of the heat exchangers of the second assembly upstream of a confluence with the first branch of the second refrigerant circuit upstream of said compressors of the second refrigerant circuit.

[0023] In order to ensure gradual and energetically efficient cooling, the first refrigerant circuit can include, in a manner analogous to the second refrigerant circuit, a branching downstream of the compressors of the first refrigerant circuit, with a first branch including at least one of said expansion valves of the first

refrigerant circuit upstream of at least one of the heat exchangers of the first heat exchanger assembly, and a second branch passing through at least one of the heat exchangers of the first heat exchanger assembly upstream of a confluence with the first branch of the first refrigerant circuit upstream of the compressors of the first refrigerant circuit.

[0024] The plant can also include a third refrigerant circuit containing a third refrigerant and also passing through one or more heat exchangers of the first heat exchanger assembly.

Brief description of the drawings

[0025] The description refers to the accompanying drawings, in which:

[0026] [Fig. 1] Figure 1 is a schematic illustration of a plant for hydrogen liquefaction according to a first embodiment.

[0027] [Fig. 2] Figure 2 is a schematic illustration of a plant for hydrogen liquefaction according to a variant of the first embodiment.

[0028] [Fig. 3] Figure 3 is a schematic illustration of a plant for hydrogen liquefaction according to a second embodiment.

Description of the embodiments

[0029] The invention will be better understood and its advantages will appear more clearly on reading the following detailed description of embodiments presented by way of non-limiting examples. The temperature and pressure values, indicated by way of example in this detailed description, are absolute values.

[0030] Figure 1 illustrates a plant for hydrogen liquefaction according to a specific embodiment. As illustrated, this plant can comprise a hydrogen feed circuit H, a first refrigerant circuit R1 and a second refrigerant circuit R2.

[0031] Starting from an inlet I, the hydrogen feed circuit H can pass successively through a first heat exchanger assembly HX11, HX12, HX13, also passed through by the first refrigerant circuit R1, and a second heat exchanger assembly HX21, HX22, HX23, HX24, HX25, HX26, also passed through by the second

refrigerant circuit R2, before ending in an expansion valve JTH, for example in the form of an adiabatic expansion valve, opening into a phase separator TH with a liquid hydrogen outlet O. It can also include a compressor for reinjection and/or an ejector EJ, disposed upstream of at least the last heat exchanger HX26, and
 5 connected to the top of the phase separator TH via a recirculation line H1 for recovering gaseous hydrogen from the phase separator TH and reinjecting it into the hydrogen feed circuit H upstream of the last heat exchanger HX26. Each of the heat exchangers can be a catalytic exchanger including a catalyst, such as trivalent iron oxide for example, for performing an ortho-para conversion in a
 10 hydrogen stream circulating in the hydrogen feed circuit H.

[0032] The first refrigerant circuit R1 can be a closed-loop refrigerant circuit, containing a refrigerant such as, for example, nitrogen and/or argon, and can comprise a plurality of compressors C1 in series, a first expansion valve JT1, for example in the form of an adiabatic expansion valve, a tank T1 and a second
 15 expansion valve E1, for example in the form of a turbine, which can be centripetal or axial.

[0033] As illustrated, this first refrigerant circuit R1 can comprise, downstream of the compressors C1 and more precisely downstream of the first heat exchanger HX11 of the first heat exchanger assembly, a branching S1 dividing the first
 20 refrigerant circuit R1 into two branches R11 and R12. The second expansion valve E1 can be disposed on the first branch R11 of the first refrigerant circuit R1 downstream of the branching S1. Downstream of the second expansion valve E1, the first branch R11 of the first refrigerant circuit R1 can pass through the second heat exchanger HX12 of the first heat exchanger assembly.

[0034] Starting from the branching S1, the second branch R12 can pass through the second heat exchanger HX12 of the first heat exchanger assembly. The first expansion valve JT1 and the tank T1 can be disposed on this second branch R12, downstream of the second heat exchanger HX12 of the first heat exchanger assembly, and the third and second heat exchangers HX13, HX12 of the first
 25 heat exchanger assembly can be passed through by this second branch R12 of the first refrigerant circuit R1 in reversed order downstream of a gas outlet from this tank T1, which then rejoins the first branch R11. The outlet of the tank T1 could, however, alternatively be a liquid outlet.
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[0035] Downstream of the confluence of the two branches R11 and R12, the first refrigerant circuit R1 can again pass through the first heat exchanger HX11 of the first heat exchanger assembly before returning to the compressors C1. The compressors C1 can be water-cooled compressors. For this purpose, it is possible, for example, to interpose intermediate heat exchangers (not shown) between the compressors C1.

[0036] The first refrigerant circuit R1 can moreover comprise at least one absorber of contaminants, such as water or oxygen, in the liquid phase of the first refrigerant. This absorber can, in particular, take the form of a powder bed for absorbing chemical species circulating in this first refrigerant circuit R1 and for which the liquefaction temperature is greater than the temperature of the liquid phase in the tank T1, and be regenerable, for example by heating. Thus, this absorber can avoid the downstream propagation of pollutants which could, by solidifying, block the first refrigerant circuit R1, in particular at the heat exchangers HX11, HX12, HX13 of the first heat exchanger assembly, or damage the expansion valves JT1, E1 and/or the compressors C1.

[0037] The second refrigerant circuit R2 can be a closed-loop refrigerant circuit, containing a refrigerant, such as hydrogen for example. This second refrigerant circuit R2 can comprise a plurality of compressors C21, C22, C23, C24, a plurality of intermediate heat exchangers IC, a first expansion valve JT2, for example in the form of an adiabatic expansion valve JT2, other expansion valves E21, E22 and E23, for example in the form of turbines, and two additional compressors C20a, C20b, each able to comprise a plurality of stages.

[0038] The intermediate heat exchangers IC can be, as illustrated, disposed directly upstream and downstream of each of the compressors C21, C22, C23, C24 in the second refrigerant circuit R2, and partially or totally immersed in a liquid phase of the first refrigerant in the tank T1, so as to enable a compression of the second refrigerant at a cryogenic temperature, for example without exceeding 150 K, preferably 113 K, in any of these compressors C21, C22, C23 and C24. Since an intermediate heat exchanger IC is disposed upstream of each of the compressors C21, C22, C23, and C24, the respective inlet temperatures of each of these compressors C21, C22, C23 and C24 could be substantially identical. Downstream of the compressors C21, C22, C23 and C24 and of the intermediate

heat exchangers IC, the second refrigerant circuit R2 can pass through the first heat exchanger HX21 of the second heat exchanger assembly. In the second refrigerant circuit R2, a branching S2 dividing the second refrigerant circuit into a first branch R21 and a second branch R22 can be disposed downstream of the first heat exchanger HX21 of the second heat exchanger assembly.

[0039] The expansion valve E21 can be disposed downstream of the branching S2, on the first branch R21 of the second refrigerant circuit R2, which can then pass through the third heat exchanger HX23 of the second heat exchanger assembly, downstream of which the expansion valves E22 and E23 can be successively disposed. The first branch R21 can then pass through the heat exchangers HX24, HX23, HX22 and HX21 in reversed order.

[0040] Downstream of the branching S2, the second branch R22 of the second refrigerant circuit R2 can successively pass through the heat exchangers HX22, HX23, HX24, HX25 of the second heat exchanger assembly. The expansion valve JT2 can be disposed on the second branch R22 of the second refrigerant circuit, downstream of these heat exchangers and upstream of the last heat exchanger HX26 of the second assembly of heat exchangers, which the second branch R22 of the second refrigerant circuit R2 passes through, before again passing through the heat exchangers HX25, HX24, HX23, HX22 and HX21 of the second heat exchanger assembly in reverse order. The additional compressors C20a, C20b can be disposed at the end of the second branch R22 of the second refrigerant circuit R2 in order to enable the stream of refrigerant from this second branch R22 of the second refrigerant circuit R2 to rejoin downstream that of the first branch R21 of the second refrigerant circuit R2 at a confluence upstream of the compressors C21, C22, C23 and C24 and intermediate heat exchangers IC.

[0041] A thermal shield (not illustrated), for example cooled with liquid nitrogen, can surround at least one part of the second refrigerant circuit R2 and of the second heat exchanger assembly HX21, HX22, HX23, HX24, HX25, HX26 in order to limit the thermal load. The second branch R22 of the second refrigerant circuit R2 can also comprise a buffer reservoir (not illustrated) downstream of the expansion valve JT2 in order to absorb the variations in speed.

[0042] In operation, this plant can implement a method for hydrogen liquefaction, wherein a gaseous hydrogen feed flow introduced by the hydrogen feed circuit H at a pressure of for example 2.1 MPa, and a temperature of for example 298 K, can be first cooled to a temperature of for example 85 K, by the heat exchangers HX11 and HX12 of the first heat exchanger assembly, then cooled again to a temperature of for example 82 K, by the last heat exchanger HX13 of the first heat exchanger assembly. In addition, in order to ensure isomeric stability of the hydrogen at this temperature and to avoid its subsequent reheating, this heat exchanger HX13 can perform, as a catalytic exchanger, an ortho-para catalytic conversion of the feed flow in order to increase the level of para-hydrogen, for example from 25 to 48%.

[0043] The stream of hydrogen to be liquefied then passes successively through the heat exchangers HX21, HX22, HX23, HX24 and HX25, where it is progressively cooled to a temperature of for example 26 K, and sees its level of para-hydrogen progressively increase to for example 98% downstream of the heat exchanger HX25. For this purpose, it can change, for example, from a level of para-hydrogen of 48% upstream of the heat exchanger HX21 to a level of 58% downstream of this heat exchanger HX21, then to a level of 67% downstream of the heat exchanger HX22, 77.5% downstream of the heat exchanger HX23, and 96% downstream of the heat exchanger HX24.

[0044] In the last heat exchanger HX26, the stream of hydrogen to be liquefied circulating via the feed circuit H can be cooled again, and its level of para-hydrogen increased again to for example 99%. Finally, its expansion, being able to be substantially adiabatic, from a pressure of for example 2 MPa, upstream of the expansion valve JTH to an outlet pressure of for example 0.2 MPa, enables its temperature to be reduced again to a temperature of for example 22.81K. Downstream of the expansion valve JTH, the stream of hydrogen circulating to the tank TH can thus be liquid, for example, up to 98%. The remaining gaseous phase can be extracted from the top of the tank TH of liquid hydrogen via the line H1, and reinjected upstream of the last heat exchanger HX26 by the ejector EJ.

[0045] In the first refrigerant circuit R1, the first refrigerant, which can in particular comprise nitrogen, can be compressed by the compressors C1, with a flow of for example 11.96 kg/s, from a pressure of for example 0.11 MPa, to a pressure of

for example 5 MPa, and this in a substantially isothermal manner at a temperature of for example 285 K. Then, this first refrigerant can be cooled to a temperature of for example 200 K, in the first heat exchanger HX11 of the first heat exchanger assembly. At the branching S1 downstream of this first heat exchanger HX11, the first refrigerant can be divided into two streams.

[0046] A first stream of the first refrigerant, which can comprise for example 70% of the total flow of the first refrigerant, can be directed through the first branch R11 of the first refrigerant circuit R1 to the expansion valve E1, where it can be expanded to a pressure of for example 0.12 MPa, in such a way as to reduce its temperature to a temperature of for example 84 K, in order to then pass through the second heat exchanger HX12 of the first heat exchanger assembly while absorbing heat there.

[0047] A second stream of the first refrigerant, which can comprise the remainder of the flow of the first refrigerant, can be directed, through the second branch R12 of the first refrigerant circuit, to the second heat exchanger HX12 of the first heat exchanger assembly, in order to be cooled there to a temperature of for example 85 K, in order to then be expanded, in particular substantially adiabatically, at the expansion valve JT1, and thus at least partially liquefy it reducing its temperature to for example 80K. Downstream of the expansion valve JT1, this at least partially liquid second stream of the first refrigerant, can be received in the tank T1, downstream of which it can again pass through, in reversed order, the third and second heat exchangers HX13, HX12 of the first heat exchanger assembly in order to be heated there before rejoining the first stream of the first refrigerant. Downstream of this confluence of the two streams of the first refrigerant, the first refrigerant can again pass through the first heat exchanger HX11 of the first heat exchanger assembly in order to be heated there before returning to the compressors C1 of the first refrigerant circuit.

[0048] In the second refrigerant circuit R2, the second refrigerant, which can in particular be hydrogen, can be compressed by the compressors C21, C22, C23, and C24 with a flow of for example 0.666 kg/s, from a pressure of for example 0.45 MPa, to a pressure of for example 2.94 MPa, and this without exceeding a maximum temperature of for example 100 K, due to the passage of the second refrigerant via the intermediate exchangers IC upstream and downstream of each

of the compressors C21, C22, C23 and C24. Each of the compressors C21, C22, C23 and C24 can be driven with a power of for example 140 kW. The respective speeds of the compressors C21, C22, C23 and C24 can be increasing in the direction of flow of the second refrigerant. Thus, compressor C21 can turn at a speed of for example 80,000 rpm, compressor C22 can turn at a second speed of for example 90,000 rpm, greater than the first speed, compressor C23 can turn at a third speed of for example 115,000 rpm, greater than the second speed, and compressor C24 can turn at a fourth speed of for example 125,000 rpm, greater than the third speed. After having been cooled to an initial temperature of for example 82 K, in the first intermediate exchanger IC, the first refrigerant can then be compressed to pressures of for example 0.72 MPa, 1.16 MPa, 1.84 MPa and 2.96 MPa respectively, downstream of the compressors C21, C22, C23 and C24, attaining a temperature of for example 100 K downstream of each of these compressors C21, C22, C23 and C24, in order to then be cooled to substantially the same initial temperature in each subsequent intermediate exchanger IC, with a pressure drop of for example 0.02 MPa in each intermediate exchanger IC.

[0049] Then, this first refrigerant can be cooled to a temperature of for example 69 K, in the first heat exchanger HX21 of the second heat exchanger assembly. The first refrigerant can then be divided into two streams at the branching S2.

[0050] A first stream of the second refrigerant, which can comprise for example 88% of the total flow of the second refrigerant, can then be directed through the first branch R21 of the second refrigerant circuit R2 to the expansion valve E21, where it can be expanded to a pressure of for example 1.9 MPa, in such a way as to reduce its temperature to a temperature of for example 60 K, in order to then pass through the third heat exchanger HX23 of the second heat exchanger assembly and to be cooled there to for example 51 K, before again being progressively expanded to a pressure of for example 0.5 MPa, at the expansion valves E22 and E23, in such a way as to again reduce its temperature to, for example 31.5 K. It can then again pass through the fourth, third, second and first heat exchangers HX24, HX23, HX22 and HX21 in reversed order in order to absorb heat there in order to obtain a temperature of for example 80 K at a pressure of for example 0.45 MPa.

[0051] A second stream of the second refrigerant, which can comprise the remainder of the flow of the second refrigerant, can be directed through the second branch R22 of the second refrigerant circuit R2, to the second, third, fourth and fifth heat exchangers HX22, HX23, HX24, HX25 of the second heat exchanger assembly, in order to be successively cooled there to a temperature of for example 26 K, in order to then be expanded, in particular substantially adiabatic, to a pressure of for example 0.17 MPa, at the expansion valve JT2, and thus to reduce its temperature there to for example 22 K. Downstream of the expansion valve JT2, this second stream of the second refrigerant can again pass through, in reversed order, the sixth, fifth, fourth, third, second and first heat exchangers HX26, HX25, HX24, HX23, HX22 and HX21 of the first heat exchanger assembly in order to absorb heat there until attaining a temperature of for example 80 K at a pressure of for example 0.15 MPa. In order to allow it to rejoin the first stream of the second refrigerant at the confluence of the two branches R21, R22 of the second circuit R2, before coming back to the compressors C21, C22, C23, C24 and the intermediate exchangers IC, the second stream can again be compressed to the same pressure as the first stream in the additional compressors C20a, C20b. The additional compressor C20a can be a two-stage compressor, driven with a power of for example 25 kW, at a speed of for example 100,000 rpm, in order to compress this second stream to a pressure of for example 0.3 MPa and a temperature of for example 113 K, while the additional compressor C20b can also be a two-stage compressor, driven with a power of for example 25 kW, at a speed of for example 100,000 rpm, in order to compress this second stream to a pressure of for example 0.45 MPa and a temperature of for example 131.5 K.

[0052] Thus, the refrigeration cycle applied in the second refrigerant circuit R2 is a two-pressure Claude cycle. Although, for this first embodiment, it has been proposed to use hydrogen as the second refrigerant, it is also possible to use other refrigerants, such as helium or even a mixture of hydrogen and neon. In this alternative embodiment, in order to avoid blocking of the second refrigerant circuit by solid neon, it would be preferable to separate the neon from the second refrigerant before its temperature descends below 25 K. For this purpose, it is possible, in particular, to condense the neon and separate it in a liquid phase. Analogously, it is also possible to use other substances alternatively or in addition

to nitrogen as first refrigerant, such as argon for example. All the pressures mentioned by way of example in this description should be understood as absolute pressures.

[0053] Figure 2 schematically illustrates a plant for hydrogen liquefaction according to a variant of the first embodiment, wherein the last heat exchanger HX13 of the first heat exchanger assembly can be incorporated in the tank T1 of the first refrigerant circuit R1, in such a way as to be partially or totally immersed there in the liquid phase of the first refrigerant. The remaining elements of the plant illustrated in figure 2 are identical or equivalent to those of the plant of figure 1 and consequently receive the same reference signs. Its operation is also analogous.

[0054] Figure 3 schematically illustrates a plant for hydrogen liquefaction according to a second embodiment, which can comprise a third refrigerant circuit R3. This third refrigerant circuit R3 can be a closed-loop refrigerant circuit, containing a third refrigerant. This third refrigerant can be a mixed refrigerant, and in particular a mixed refrigerant comprising hydrocarbons. Such a mixed refrigerant can be formed by a mixture of nitrogen, methane, ethane, propane and butane.

[0055] The third refrigerant circuit R3 can comprise an assembly of compressors C3 upstream of a first phase separator T31, which can form a first branching of the third refrigerant circuit R3, dividing it into a first branch R31, which can comprise an additional compressor C3', and a second branch R32, which can comprise a pump P3. These two branches R31, R32 can rejoin each other downstream of the compressor C3' and the pump P3, upstream of a second phase separator T32, which can form a second branching of the third circuit refrigerant R3, dividing it into a third branch R33 and a fourth branch R34.

[0056] The third branch R33 can comprise an expansion valve JT33, for example in the form of an adiabatic expansion valve, and pass through, both upstream and downstream of this expansion valve JT33, a first heat exchanger HX10 of the first heat exchanger assembly, which can comprise four heat exchangers HX10, HX11, HX12 and HX13 in this second embodiment, in order to then return upstream of the assembly of compressors C3.

[0057] The fourth branch R34 can likewise pass through the first heat exchanger HX10 of the first heat exchanger assembly, upstream of a third phase separator T33, which can form a third branching of the third refrigerant circuit R3, dividing the fourth branch R34 into a fifth branch R35 and a sixth branch R36.

5 [0058] The fifth branch R35 can comprise an expansion valve JT35, for example in the form of an adiabatic expansion valve, and pass through, both upstream and downstream of this expansion valve JT35, the second heat exchanger HX11 of the first heat exchanger assembly.

10 [0059] The sixth branch R36 can likewise comprise an expansion valve JT36, for example in the form of an adiabatic expansion valve, and successively pass through, upstream of this expansion valve, the second and third heat exchangers HX11, HX12 of the first heat exchanger assembly, in order to pass through it again, in reversed order, downstream of the expansion valve JT36, before rejoining the fifth branch R35.

15 [0060] The first heat exchanger HX10 of the first heat exchanger assembly can again be passed through by the fourth branch R34 downstream of the confluence of the fifth and sixth branches R35, R36, upstream of a confluence of the fourth branch R34 with the third branch R33 upstream of the return to the compressors C3.

20 [0061] Compared to that of the first embodiment, the first refrigerant circuit R1 can be simplified, and form only a single loop passing through, downstream of the compressors C1, the first to third heat exchangers HX10, HX11, HX12 in a first direction, in order to then pass through them in reverse order downstream of a single expansion valve JT1, which can be in the form of an adiabatic expansion valve, and the tank T1, before coming back to the inlet of the compressors C1. As
25 in the variant of the first embodiment, a last heat exchanger HX13 of the first heat exchanger assembly HX10, HX11, HX12, HX13 passed through by the hydrogen feed circuit H can be incorporated in the tank T1 in order to be partially or totally immersed there in the liquid phase of the first refrigerant.

30 [0062] The remaining elements of the plant according to this second embodiment can be identical or equivalent to those of the first embodiment and consequently receive the same reference signs.

[0063] In operation, in the third refrigerant circuit R3, the third refrigerant can first be compressed in the compressors C3, for example from 0.1 MPa to 1.1 MPa. At this pressure, a liquid phase can appear, which can be separated from the gaseous phase of the third refrigerant in the first phase separator T31 of the third refrigerant circuit R3, in order to be directed to the second branch R32 of the third refrigerant circuit R3 and to be pumped there by the pump P3 to a pressure of for example 2.2 MPa, while the gaseous phase can be directed through the first branch R31, in order to be compressed there by the additional compressor C3' to the same pressure as the liquid phase of the second branch R32. The separation of the phases and the pumping of the liquid phase by a pump, for the last increase in pressure, enables the energy consumption for this step to be limited.

[0064] Downstream of the confluence of the first and second branches R31, R32 of the third refrigerant circuit R3, liquid and gaseous phases can be separated again in the second phase separator T32, in order to direct the liquid phase through the third branch R33 and the gaseous phase through the fourth branch R34.

[0065] The liquid fraction of the third refrigerant directed through the third branch R33 of the third refrigerant circuit R3 can first be cooled to a temperature of for example 182 K, in the first heat exchanger HX10 of the first heat exchanger assembly, in order to then be expanded, in particular substantially adiabatically, to a pressure of for example 0.1 MPa, in the expansion valve JT33 of the third branch R33, before again passing through the first heat exchanger HX10 of the first heat exchanger assembly in order to absorb heat there, and then to be conducted again to the compressors C3.

[0066] The gaseous fraction of the third refrigerant directed through the fourth branch R34 of the third refrigerant circuit R3 can likewise first be cooled to a temperature of for example 182 K, in the first heat exchanger HX10 of the first heat exchanger assembly in order to be partially condensed there before arriving at the third phase separator T33, wherein liquid and solid phases can again be separated in order to be directed, respectively, through the fifth and sixth branches R35, R36 of the third refrigerant circuit.

[0067] The liquid fraction of the third refrigerant directed through the fifth branch R35 of the third refrigerant circuit R3 can be cooled to a temperature of for example

115 K in the second exchanger HX11 of the first heat exchanger assembly, in order to then be expanded, in particular substantially adiabatically, to a pressure of for example 0.1 MPa, in the expansion valve JT35 of the fifth branch R35, before again passing through, in reversed order, the second and first heat exchangers HX11, HX10 of the first heat exchanger assembly in order to absorb heat there, and to then be conducted again to the compressors C3.

[0068] The gaseous fraction of the third refrigerant directed through the sixth branch R36 of the third refrigerant circuit R3 can be cooled to a temperature of for example 82 K on passing through the second and third heat exchangers HX11, HX12 of the first heat exchanger assembly, in order to then be expanded, in particular substantially adiabatically, to a pressure of for example 0.1 MPa, in the expansion valve JT36 of the sixth branch R36, before again passing through, in reversed order, the third, second and first heat exchangers HX12, HX11, HX10 of the first heat exchanger assembly in order to absorb heat there, and to then be conducted again to the compressors C3.

[0069] In the first refrigerant circuit R1, the first refrigerant can be compressed, for example from 0.1 MPa to 4 MPa, in the compressors C1, and then cooled to for example 90 K, on passing through the first, second and third heat exchangers HX10, HX11, HX12 of the first heat exchanger assembly. It can then be expanded, in particular substantially adiabatically, in the single expansion valve JT1 of the first refrigerant circuit R1, in such a way as to reduce its temperature to for example 78 K and at least partially liquefy it before arriving in the tank T1.

[0070] A gaseous fraction of the first refrigerant can leave the tank T1 in order to pass through, in reversed order, the third, second and first heat exchangers HX12, HX11, HX10 of the first heat exchanger assembly in order to absorb heat there before returning to the compressors C1 of the first refrigerant circuit.

[0071] In the second refrigerant circuit R2, the second refrigerant can circulate in a manner substantially analogous to the first embodiment, while gaseous hydrogen introduced into the hydrogen feed circuit H can first be cooled to for example 90 K, on passing through the first, second and third heat exchangers HX10, HX11 and HX12 of the first heat exchanger assembly, in order to then be cooled to 80 K on passing through the last heat exchanger HX13 of the first heat exchanger

assembly which, as in the first embodiment, can be a catalytic exchanger capable of performing, as a catalytic exchanger, an ortho-para catalytic conversion of the feed flow in order to increase there the level of para-hydrogen, for example from 25 to 48%. The subsequent steps of the cooling and liquefaction of the hydrogen circulating through the hydrogen feed circuit H can be analogous to that of the first embodiment.

[0072] Although the present invention has been described by referring to specific embodiments, it is obvious that various modifications and changes can be made to these examples without going beyond the general scope of the invention as defined by the claims. In addition, the individual features of different embodiments mentioned can be combined in additional embodiments. Consequently, the description and the drawings should be considered as illustrating rather than limiting.

Claims

[Claim 1] A method for hydrogen liquefaction comprising at least:

5 a pre-cooling step, wherein a hydrogen feed flow is cooled by a first refrigerant,

a cooling step, wherein the hydrogen feed flow is cooled by a second refrigerant, and

a step of expanding, in particular substantially adiabatically expanding, the hydrogen feed flow,

10 and wherein each of the first and second refrigerants is successively subjected to at least one compression and to at least one expansion in order to cool it, and a liquid phase of the first refrigerant cools the second refrigerant between at least three stages of a compression of the second refrigerant, so that the second refrigerant does not exceed a temperature of
15 150 K, preferably 113 K, during said compression of the second refrigerant.

[Claim 2] The method for hydrogen liquefaction according to claim 1, wherein the first refrigerant comprises nitrogen and/or argon.

20 [Claim 3] The method for hydrogen liquefaction according to either of claims 1 or 2, wherein the liquid phase of the first refrigerant cools the second refrigerant upstream of each of said at least three compression stages of the second refrigerant.

25 [Claim 4] The method for hydrogen liquefaction according to any one of claims 1 to 3, wherein the second refrigerant comprises hydrogen, neon and/or helium.

30 [Claim 5] The method for hydrogen liquefaction according to any one of claims 1 to 4, wherein the second refrigerant is divided into a first stream which is subject to an expansion in order to cool it, and a second stream which is

cooled by the first stream of the second refrigerant after the expansion of the first stream of the second refrigerant.

[Claim 6] The method for hydrogen liquefaction according to claim 5, wherein

5 the second stream of the second refrigerant is subject to an expansion, in particular to a substantially adiabatic expansion, after having been cooled by the first stream of the second refrigerant.

[Claim 7] The method for hydrogen liquefaction according to any one of claims 1

10 to 6, wherein the first refrigerant is divided into a first stream which is subject to an expansion in order to cool it and a second stream which is cooled by the first stream of the first refrigerant after the expansion of the first stream of the first refrigerant.

[Claim 8] The method for hydrogen liquefaction according to claim 7, wherein

15 the second stream of the first refrigerant is subject to an expansion, in particular to a substantially adiabatic expansion, after having been cooled by the first stream of the first refrigerant.

[Claim 9] The method for hydrogen liquefaction according to any one of claims 1

20 to 8, wherein the hydrogen feed flow is also cooled by a third refrigerant during the precooling step.

[Claim 10] A hydrogen liquefaction plant comprising, at least:

25 a hydrogen feed circuit (H),
a first refrigerant circuit (R1) containing a first refrigerant,
a second refrigerant circuit (R2) containing a second refrigerant,
a first heat exchanger assembly (HX10, HX11, HX12, HX13) passed through
by the hydrogen feed circuit (H) and by the first refrigerant circuit (R1),
30 a second heat exchanger assembly (HX21, HX22, HX23, HX24, HX25, HX26)
passed through by the second refrigerant circuit (R2) and by the hydrogen
feed circuit (H) downstream of the first heat exchanger assembly (HX10,

HX11, HX12, HX13), and

an expansion valve, for example an adiabatic expansion valve (JTH), passed through by the hydrogen feed circuit (H) downstream of the second heat exchanger assembly (HX21, HX22, HX23, HX24, HX25, HX26),

5 wherein the first refrigerant circuit (R1) includes one or more compressors (C1) and one or more expansion valves (E1, JT1), and the second refrigerant circuit (R2) comprises at least three compressors (C21, C22, C23, C24) and a cooling device comprising a plurality of intermediate exchangers (IC)

10 interposed between said at least three compressors (C21, C22, C23, C24) of the second refrigerant circuit (R2) so as to carry out at least three compressions of the second refrigerant without exceeding a temperature of 150 K, preferably 113 K, and one or more expansion valves (JT2, E21, E22, E23), the cooling device being configured to cool the second refrigerant in the second refrigerant circuit (R2) with a liquid phase of the first refrigerant in the first refrigerant circuit (R1), in particular in a tank (T1) of the first refrigerant circuit (R1).

[Claim 11] The hydrogen liquefaction plant according to claim 10, wherein one of said intermediate exchangers (IC) is disposed upstream of each of said at least three compressors (C21, C22, C23, C24) of the second refrigerant circuit.

[Claim 12] The hydrogen liquefaction plant according to either of claims 10 or 11, wherein said at least three compressors (C21, C22, C23, C24) of the second refrigerant circuit (R2) have magnetic bearings, in particular active magnetic bearings.

[Claim 13] The hydrogen liquefaction plant according to any one of claims 10 to 12, wherein said at least three compressors (C21, C22, C23, C24) of the second refrigerant circuit (R2) are centrifugal compressors.

[Claim 14] The hydrogen liquefaction plant according to any one of claims 10 to 13, wherein at least one heat exchanger (HX13, HX21, HX22, HX23, HX24, HX25, HX26) of the first heat exchanger assembly or of the second heat exchanger assembly is a catalytic exchanger.

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[Claim 15] The hydrogen liquefaction plant according to any one of claims 10 to 14, wherein the second refrigerant circuit (R2) includes a branching (S2), downstream of said at least three compressors (C21, C22, C23, C24) of the second refrigerant circuit (R2), with a first branch (R21) including one or more of said expansion valves (E21, E22, E23) of the second refrigerant circuit (R2) and passing through, downstream, at least one of the heat exchangers (HX21, HX22, HX23, HX24) of the second assembly, and a second branch (R22) passing through at least one of the heat exchangers (HX21, HX22, HX23, HX24, HX25, HX26) of the second assembly before rejoining the first branch (R21) of the second refrigerant circuit (R2) upstream of said compressors (C21, C22, C23) of the second refrigerant circuit (R2).

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[Claim 16] The hydrogen liquefaction plant according to any one of claims 10 to 15, wherein the first refrigerant circuit (R1) includes a branching (S1), downstream of the compressors (C1) of the first refrigerant circuit, with a first branch (R11) including at least one of said expansion valves (E1) of the first refrigerant circuit (R1) and passing through, downstream, at least one of the heat exchangers (HX12) of the first heat exchanger assembly (HX11, HX12, HX13), and a second branch (R12) passing through at least one of the heat exchangers (HX12, HX13) of the first heat exchanger assembly (HX11, HX12, HX13) before rejoining the first branch (R11) of the first refrigerant circuit (R1) upstream of the compressors (C1) of the first refrigerant circuit (R1).

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[Claim 17] The hydrogen liquefaction plant according to any one of claims 10 to 16, further including a third refrigerant circuit (R3) containing a third refrigerant and also passing through one or more heat exchangers (HX10,

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HX11, HX12) of the first heat exchanger assembly (HX10, HX11, HX12, HX13).

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