

DEVICE AND METHOD FOR LIQUEFYING A GAS

Technical field of the invention

The present invention relates to a device for liquefying a gas and a method for liquefying a gas. It applies, in particular, to the field of liquefying a flow of dihydrogen.

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State of the art

The liquefaction of dihydrogen is an energy-intensive process with a theoretical minimum energy consumption of 3.9 kWh per kilogramme of liquid hydrogen produced. The industrial cycles in use today consume between 11 and 13 kWh/kgLH₂. When dihydrogen is used as a cooling fluid or refrigerant, more than half of the consumption can be allocated to its compression. Improving the energy consumption of the hydrogen compressors is therefore crucial for reducing the final cost of the liquefaction of hydrogen.

Dihydrogen exists naturally in two forms according to the number of spins of its two protons, orthohydrogen ("o-H₂") and parahydrogen ("p-H₂"). The equilibrium composition of dihydrogen changes with the temperature, as shown in figure 1. In figure 1, the X-axis 110 measures the temperature in degrees Kelvin and the Y-axis 105 measures the percentage of parahydrogen in the hydrogen. At ambient temperature, the dihydrogen is composed of 75% orthohydrogen and 25% parahydrogen (this composition is subsequently called normal hydrogen) whereas at approximately 20 K, the liquefaction temperature, it is almost 100% parahydrogen. If normal hydrogen is liquefied and stored, a slow conversion to the parahydrogen form occurs (over several days). The heat generated by this conversion vaporises a portion of the liquid stored, and thus will generate a loss.

In the case where dihydrogen has the role of refrigerant, the temperature of the refrigerant fluid varies across the refrigeration cycle and the composition changes slowly because of the natural conversion. In addition, although the volumetric properties of orthohydrogen and parahydrogen are similar, the calorimetric properties are substantially different. Therefore the natural exothermic conversion (orthohydrogen to parahydrogen) and the differences in physical properties between the two forms affect the performance levels of the refrigeration cycle and generate increased consumption at the level of the compressors of a closed refrigeration cycle. This effect is even more significant when the compression is performed at low temperature and/or the dihydrogen is stored at low temperature (e.g. in an intermediate storage).

For open hydrogen liquefaction cycles, such as, for example, the one described in patent US7559213, the composition of the dihydrogen when it is used as a refrigerant is directly dependent on the state of the conversion of the hydrogen flow to be liquefied and this composition does not vary over time. In effect, the hydrogen recycled in the cycle has a composition of 99% parahydrogen

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5 and is mixed in a fixed proportion over time with the dihydrogen to be liquefied whose composition is normal.

Some closed liquefaction cycles use dihydrogen as refrigerant. Beyond 184 K (-89°C) the equilibrium composition varies little, and because of this the changes in the composition and its impact are largely negligible.

10 Recent developments have highlighted liquefaction cycles where the average temperature of the hydrogen used as a refrigerant is below 184 K (-89°C). In "Advanced precooling for optimized hydrogen liquefaction", H2Tech, March 2021, Howe, Skinner and Finn present a closed cycle compressing hydrogen at low temperature, i.e. at around 120 K (-153°C). Patent application FR2105720 proposes a closed cycle where the hydrogen used as refrigerant does not exceed a
15 temperature of 150 K (-123°C). As a consequence, the hydrogen is subject to a slow conversion to a state different from normal hydrogen. In "Large scale hydrogen liquefaction in combination with LNG re-gasification", 2006, Kuendig mentions that the refrigerant will comprise between 30% and 50% parahydrogen after a long period of operation without giving an order of magnitude.

For information, other uses of the conversion have been proposed in the literature, such as
20 patent application FR2006278, which presents a system converting the parahydrogen of the boil-off gas coming from the storage of liquid hydrogen downstream from the liquefier so as to use the frigories generated to cool the throughput of hydrogen to be liquefied, or the publication "Enhanced dormancy due to para-to-ortho hydrogen conversion in insulated cryogenic pressure vessels for automotive applications" in which J.K. Peng uses the conversion of parahydrogen into
25 orthohydrogen to slow the pressure rise of a storage of cryo-compressed hydrogen.

The open hydrogen liquefaction cycles solve the issue of the change in the composition of the hydrogen by means of the conversion step for the hydrogen to be liquefied. However, these cycles have low energy efficiency.

The literature proposes no solution for controlling the composition of the hydrogen
30 refrigerant for a closed refrigeration cycle. As a result, the composition of the refrigerant changes slowly, which has unforeseen and undesirable effects on the heat exchanges and performance of the compression and expansion steps.

In addition, this change is heavily dependent on the methods considered, exterior conditions and load factor of the installation.

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Presentation of the invention

The present invention aims to remedy all or part of these drawbacks.

To this end, according to a first aspect, the present invention envisages a device according to claim 1.

Thanks to these provisions, the hydrogen liquefaction cycle controls the composition of the hydrogen used as refrigerant, for example by using at least one catalytic reactor in the refrigeration cycle set to a selected temperature, to optimise the properties of the refrigerant and reduce the

5 energy consumption of the device by having an operating equilibrium composition that is different from the natural equilibrium composition.

These provisions make it possible to convert the normal hydrogen to a target composition during the initialisation of the refrigeration cycle and to counter the natural conversion taking place throughout the lifespan of the installation. Because of this, the physical properties of the refrigerant
10 remain unchanged and the losses are reduced, preventing excessive energy consumption. In some optional embodiments, the closed refrigeration circuit is configured such that the dihydrogen refrigerant has, on input to the catalytic reactor, a temperature essentially equal to the average temperature of the dihydrogen refrigerant in the closed circuit.

These embodiments make it possible to minimise the thermal impact of the conversion from
15 orthohydrogen to parahydrogen. In some optional embodiments, the catalytic reactor is positioned on a hot branch of the closed refrigeration circuit.

These embodiments make it possible to optimise the parahydrogen content by converting most of the hydrogen refrigerant during each passage in the reactor. These embodiments make it possible to minimise the thermal impact of the conversion if the conversion takes place on the hot
20 branch instead of the cold branch that has the role of coolant.

In some optional embodiments, the catalytic reactor is configured to operate at a temperature between 31 K and 184 K. These embodiments enable an optimum energy efficiency of the device.

In some optional embodiments, the maintenance means is configured to maintain the
25 proportion of parahydrogen in the internal composition of the dihydrogen refrigerant flow between 27% and 96%. These embodiments enable an optimum energy efficiency of the device.

In some optional embodiments, the maintenance means comprises a bypass of the catalytic reactor configured to operate a predefined throughput ratio between the flow passing through the reactor and the flow passing through the bypass. These embodiments enable a dynamic
30 adjustment, proportional to the throughputs bypassed and passing through the reactor, of the composition of the dihydrogen.

In some optional embodiments, the closed dihydrogen refrigerant circuit is configured to maintain an average temperature of the dihydrogen refrigerant between 31 K and 184 K. These embodiments enable an optimum energy efficiency of the device.

In some optional embodiments, the device that is the subject of the present invention comprises a circuit for pre-cooling the gas to be liquefied, this pre-cooling circuit comprising a heat exchanger for exchanging heat between a pre-cooling fluid flow and the dihydrogen refrigerant flow. These embodiments enable an optimum energy efficiency of the device.

35 In some optional embodiments, the gas to be liquefied is a flow comprised essentially of dihydrogen.

In some optional embodiments, at least one catalytic reactor is integrated into a heat exchanger. Integrating the catalyser into a heat exchanger makes it possible to obtain a continuous

conversion during the descent in temperature of the hydrogen to be liquefied, which reduces the overall energy consumption of the liquefaction method.

In addition, this catalytic exchanger for the dihydrogen refrigerant flow makes it possible to eliminate one catalytic reactor, which reduces the cost and complexity of the overall method.

In some optional embodiments, the closed refrigeration circuit comprises a stage of intercooling compression and at least one stage of compression at a temperature below -40°C for the dihydrogen refrigerant. These provisions make it possible to limit the rise in temperature of the dihydrogen refrigerant and therefore to lower the average temperature in the cooling circuit.

In some optional embodiments, the catalytic reactor is positioned on a cold branch of the closed refrigeration circuit. These embodiments make it possible to lower the overall average temperature of the refrigerant flow in the closed conveyance circuit.

In some optional embodiments, the closed refrigeration circuit comprises at least one compressor of the dihydrogen refrigerant at ambient temperature and a storage tank for the liquid dihydrogen refrigerant.

In some optional embodiments, the catalytic reactor utilises a catalyser comprising a member of the iron oxides family, preferably Fe_2O_3 .

According to a second aspect, the present invention envisages a method for liquefying a gas, which comprises:

- a step of conveying gas to be liquefied, comprising at least one step of exchanging heat between the gas to be liquefied and a dihydrogen refrigerant flow;

- a step of conveying, in a closed refrigeration circuit, the dihydrogen refrigerant flow, the conveying step comprising a step of maintaining an internal composition of the dihydrogen refrigerant at a ratio of parahydrogen to orthohydrogen that is lower or higher than the ratio corresponding to a natural equilibrium composition in the closed refrigerant flow circuit, this maintenance means comprising a catalytic reaction step to convert some of the orthohydrogen from the dihydrogen refrigerant into parahydrogen or vice versa.

The advantages of the method that is the subject of the present invention are similar to those of the device that is the subject of the present invention.

Brief description of the figures

Other advantages, aims and particular features of the invention will become apparent from the non-limiting description that follows of at least one particular embodiment of the device and method that are the subjects of the present invention, with reference to drawings included in an appendix, wherein:

Figure 1 represents, schematically, the changes in the proportion of parahydrogen in the internal composition of the dihydrogen as a function of the temperature;

Figure 2 represents, schematically, a first particular embodiment of the device that is the subject of the invention;

5 Figure 3 represents, schematically, a second particular embodiment of the device that is the subject of the invention;

 Figure 4 represents, schematically, a third particular embodiment of the device that is the subject of the invention;

10 Figure 5 represents, schematically, a fourth particular embodiment of the device that is the subject of the invention;

 Figure 6 represents, schematically, a fifth particular embodiment of the device that is the subject of the invention;

 Figure 7 represents, schematically, a sixth particular embodiment of the device that is the subject of the invention;

15 Figure 8 represents, schematically, a seventh particular embodiment of the device that is the subject of the invention;

 Figure 9 represents, schematically and in the form of a logic diagram, a series of steps of a particular embodiment of the method that is the subject of the invention; and

20 Figure 10 represents, schematically, an eighth particular embodiment of the device that is the subject of the invention.

Description of the embodiments

25 The present description is given in a non-limiting way, in which each characteristic of an embodiment can be combined with any other characteristic of any other embodiment in an advantageous way.

 As can be seen from reading the present description, different inventive concepts can be implemented by one or more methods or devices described below, several examples of which are given here. The actions or steps carried out in the framework of realising the method or device can be ordered in any appropriate way. As a consequence, it is possible to construct embodiments in
30 which the actions or steps are carried out in a different order from the one shown, which can include executing some acts simultaneously, even if they are presented as sequential acts in the embodiments shown.

 The indefinite articles "one" or "a", as used in the description and in the claims, must be understood as meaning "at least one", except when the contrary is clearly indicated.

35 The expression "and/or", as it is used in the present document and in the claims, must be understood as meaning "one or other, or both" of the elements thus connected, i.e. elements that are present conjunctively in some cases and disjunctively in other cases. The multiple elements listed with "and/or" must be interpreted in the same way, i.e. "one or more" of the elements thus connected. Other elements can possibly be present, other than the elements specifically identified
40 by the clause "and/or", whether or not they are linked to these specifically identified elements. Therefore, as a non-limiting example, a reference to "A and/or B", when it is used in conjunction with open-ended language such as "comprising", can refer, in one embodiment, to A only (possibly

5 including elements other than B); in another embodiment, to B only (possibly including elements other than A); in yet another embodiment, to A and B (possibly including other elements); etc.

As used here in the description and in the claims, "or" must be understood as having the same meaning as "and/or" as defined above. For example, when separating elements in a list, "or" or "and/or" must be interpreted as being inclusive, i.e. the inclusion of at least one, but also of more
10 than one, of a number or a list of elements, and, optionally, of additional elements not listed. Only the terms clearly indicating the contrary, such as "only one of" or "exactly one of", or, when they are used in the claims, "consisting of", refer to the inclusion of a single element of a number or a list of elements. In general, the term "or" as it is used here must only be interpreted as indicating exclusive alternatives (i.e. "one or the other, but not both") when it is preceded by exclusivity terms,
15 such as "either", "one of", "only one of", or "exactly one of".

As used here in the present description and in the claims, the expression "at least one", in reference to a list of one or more elements, must be understood as meaning at least one element chosen from among one or more elements in the list of elements, but not necessarily including at least one of each element specifically listed in the list of elements and not excluding any
20 combination of elements in the list of elements. This definition also allows the optional presence of elements other than the elements specifically identified in the list of elements to which the expression "at least one" refers, whether or not they are linked to these specifically identified elements. Therefore, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B" or, equivalently, "at least one of A and/or B"), can refer, in one embodiment, to at
25 least one, possibly including more than one, A, with no B present (and possibly including elements other than B); in another embodiment, to at least one, possibly including more than one, B, with no A present (and possibly including elements other than A); in yet another embodiment, to at least one, possibly including more than one, A and at least one, possibly including more than one, B (and possibly including other elements); etc.

30 In the claims, and also in the description below, all the transitive expressions such as "comprising", "including", "bearing", "having", "containing", "involving", "made of", "formed of" and others, must be understood as being open, i.e. meaning including, but not limited to. Only the transitive expressions "consisting of" and "consisting essentially of" must be understood as closed or semi-closed expressions, respectively.

35 Note that the figures are not to scale.

The gas 51 to be liquefied can be any type generally liquefied. Preferably, this gas 51 is dihydrogen.

The refrigerant flow is defined as comprising at least dihydrogen refrigerant. The proportion of dihydrogen refrigerant depends on the specific use of the present invention. In some variants,
40 the proportion of dihydrogen refrigerant in the refrigerant flow is at least 30%. In some variants, the proportion of dihydrogen refrigerant in the refrigerant flow is at least 50%. In some variants, the proportion of dihydrogen refrigerant in the refrigerant flow is at least 70%. In some variants, the

proportion of dihydrogen refrigerant in the refrigerant flow is at least 90%. In some variants, the proportion of dihydrogen refrigerant in the refrigerant flow is at least 99%. In the description that follows, the terms "refrigerant flow" and "dihydrogen refrigerant" are used interchangeably.

The dihydrogen refrigerant 52 can have the liquefied dihydrogen 51 as source or can come from a third source.

The term "hot branch" of a closed circuit refers to at least one portion of this circuit in which the temperature of the fluid conveyed decreases.

The term "cold branch" of a closed circuit refers to at least one portion of this circuit in which the temperature of the fluid conveyed increases.

Figure 2, which is not to scale, shows a schematic view of an embodiment of the device 200 that is the subject of the present invention. This device 200 for liquefying a gas 51 comprises:

- a circuit 55 for conveying gas to be liquefied, the circuit comprising at least one heat exchanger 204 for exchanging heat between the gas 51 to be liquefied and a refrigerant flow 52 comprising at least dihydrogen refrigerant;
- a closed refrigeration circuit 210 configured to essentially convey the refrigerant flow, the closed refrigeration circuit comprising a means 215 for maintaining an internal composition of the dihydrogen refrigerant at a ratio of parahydrogen to orthohydrogen that is lower or higher than the ratio corresponding to a natural equilibrium composition in the closed refrigerant flow circuit, this maintenance means comprising a catalytic reactor 220 configured to convert some of the orthohydrogen from the dihydrogen refrigerant flow into parahydrogen or vice versa.

The conveyance circuit 55 is, for example, formed of a set of pipes configured to convey the gas 51 to be liquefied, the gas 51 coming from a source (not shown) and being conveyed to a fixed or mobile storage 56. This conveyance circuit 55 is configured to convey the gas 51 through at least one heat exchanger, 201, 202, 203, 204, 205, 206, 207, 208 and/or 209. Each exchanger, 201, 202, 203, 204, 205, 206, 207, 208 and/or 209, can belong to a pre-cooling and/or cooling circuit. The number and arrangement of heat exchangers, 201, 202, 203, 204, 205, 206, 207, 208 and/or 209, are dependent upon the desired configuration for the device 200, desired specifications for the gas 51 on output from this device 200 and desired energy performance for the device 200.

In some embodiments, the gas 51 to be liquefied is dihydrogen in gaseous form, having a mass flow rate of 0.116 kg/s, a pressure of 21 bar and a temperature of 298 K.

The embodiments, 200, 300, 400, 500, 600, 700, 1100, shown in figures 2 to 7 and 10 each comprise nine heat exchangers in succession. In these figures 2 to 7 and 10, the heat exchangers are organised as follows:

- the flow of gas 51 first passes through a pre-cooling section, comprising:
 - a first exchanger, 201, 301, 401, 501, 601, 701;
 - a second exchanger, 202, 302, 402, 502, 602, 702; and
 - a third exchanger, 203, 303, 403, 503, 603, 703,
- the flow of gas 51 then passes through a cooling section, comprising:

- 5 - a fourth exchanger, 204, 304, 404, 504, 604, 704;
- a fifth exchanger, 205, 305, 405, 505, 605, 705;
- a sixth exchanger, 206, 306, 406, 506, 606, 706;
- a seventh exchanger, 207, 307, 407, 507, 607, 707;
- an eighth exchanger, 208, 308, 408, 508, 608, 708; and
- 10 - a ninth exchanger, 209, 309, 409, 509, 609, 709,

- the flow of liquefied gas 51 is then routed towards the storage 56, optionally first passing through an expansion valve 53, referred to as a "Joule-Thomson" expansion valve.

The storage 56 can be a temporary storage for the separation of the boil-off gas and the liquefied gas 51.

As can be understood, for example, the feed flow is comprised of normal hydrogen (25% parahydrogen and 75% orthohydrogen) having a pressure of 21 bar, a temperature of 298 K (25°C) and a mass flow rate of 0.116 kg/s. The flow 51 is first cooled to 83 K (-190°C) by the action of two heat exchangers. This flow 51 next enters into a catalytic heat exchanger performing the first step of the ortho-para conversion. The flow 51 exits from the pre-cooling portion at a temperature of 80 K (-193°C) and a composition formed of 49 % parahydrogen.

- In the cooling portion, the feed flow 51 reaches a temperature of 22 K (-251°C) and a composition of 99% parahydrogen through a sequence of six catalytic heat exchanger in series.
- 15 The final liquefaction step is performed with an expansion valve that lowers the pressure to 2 bars. The liquid portion of the flow (98%) exits from the device and the gaseous portion remaining is conveyed to an exhaust gas management system.

Figure 8 shows a variant of the circuit 55 for conveying gas 51, the circuit comprising eight heat exchangers. In this variant, the heat exchangers are organised as follows:

- 20 - the flow of gas 51 first passes through a pre-cooling section, comprising:
 - a first exchanger 801; and
 - a second exchanger 802,
- the flow of gas 51 then passes through a cooling section, comprising:
 - a third exchanger 803;
 - 25 - a fourth exchanger 804;
 - a fifth exchanger 805;
 - a sixth exchanger 806;
 - a seventh exchanger 807; and
 - an eighth exchanger 808,
- 30 - the flow of liquefied gas 51 is then routed towards the storage 56.

With regard to the embodiments shown in figures 2 to 8 and 10, each heat exchanger is, for example, a plate exchanger exchanging heat between a fluid referred to as "hot" and a fluid referred to as "cold". In each such heat exchanger, the gas 51 to be liquefied acts as a hot fluid. The cold fluid depends on the variants of implementation. For example, in figures 2 to 8 and 10,

the exchangers of the cooling section utilise the dihydrogen refrigerant as cold fluid, while the exchangers of the pre-cooling section utilise the dihydrogen refrigerant and a pre-cooling fluid.

Therefore, as can be understood, all or part of the heat exchangers are passed through by the closed refrigeration circuit 210. The refrigeration circuit 210 is, for example, formed of a set of pipes configured to convey the dihydrogen refrigerant 52. This conveyance circuit 210 is configured to convey the dihydrogen refrigerant 52 through at least one heat exchanger, 201, 202, 203, 204, 205, 206, 207, 208 and/or 209. The configuration of the refrigeration circuit 210 is dependent upon the desired energy performance for the device 200 and operating conditions specified for this device 200.

In some embodiments, the dihydrogen refrigerant 52 is configured to have a temperature between 171 K and 22 K, this dihydrogen refrigerant 52 being configured to cool the gas 51 to be liquefied.

In the embodiment of the device 200 shown in figure 2, the refrigeration circuit 210 is a closed circuit that comprises:

- a branch referred to as "hot", in which the refrigeration circuit 210 passes successively through:
 - the second heat exchanger 202;
 - the third heat exchanger 203;
 - the fourth heat exchanger 204;
 - the means 215 for maintaining an internal composition of the dihydrogen;
 - the fifth heat exchanger 205;
 - the sixth heat exchanger 206;
 - the seventh heat exchanger 207;
 - the eighth heat exchanger 208; and
- an expansion valve 211,
- a branch referred to as "cold", formed of two portions:
 - a first portion, having for source the output from the expansion valve 211, in which the refrigeration circuit 210 passes successively through:
 - the ninth heat exchanger 209;
 - the eighth heat exchanger 208;
 - the seventh heat exchanger 207;
 - the sixth heat exchanger 206;
 - the fifth heat exchanger 205;
 - the fourth heat exchanger 204;
 - a first compressor 212;
 - a second compressor 213, the dihydrogen refrigerant on output from the second compressor 213 being supplied to the second heat exchanger 202, and

- 5 - a second portion, having for source a deviation located at the outlet from the maintenance means 215, in which the refrigeration circuit 210 passes successively through:
- a first expander 214;
 - the sixth heat exchanger 206;
 - a second expander 216;
 - the seventh heat exchanger 207;
 - the sixth heat exchanger 206;
 - the fifth heat exchanger 205;
 - the fourth heat exchanger 204, the dihydrogen refrigerant on output from
- 10 the fourth heat exchanger 204 being supplied to the second compressor 213.

In the embodiment of the device 300 shown in figure 3, the refrigeration circuit 310 is a closed circuit, similar to the refrigeration circuit 210 as shown in figure 2, which has the following variants:

- 15 – the maintenance means 315 is positioned on the first portion of the cold branch, between the sixth heat exchanger 306 and the fifth heat exchanger 305; and
- the second portion of the cold branch has for source a deviation on outlet from the fourth heat exchanger 304 along the hot branch.

In the embodiment of the device 400 shown in figure 4, the refrigeration circuit 410 is a closed circuit, similar to the refrigeration circuit 210 as shown in figure 2, in which the maintenance means 415 comprises two catalytic reactors, 420 and 421, located either side of the fourth heat exchanger 404 along the hot branch.

In the embodiment of the device 500 shown in figure 5, the refrigeration circuit 510 is a closed circuit, similar to the refrigeration circuit 210 as shown in figure 2, which has the following variants:

- the maintenance means 515 is positioned on the hot branch, between the fifth heat exchanger 505 and the sixth heat exchanger 506; and
- the second portion of the cold branch has for source a deviation on outlet from the fourth heat exchanger 304 along the hot branch.

30 In the embodiment of the device 700 shown in figure 7, the refrigeration circuit 710 is a closed circuit, similar to the refrigeration circuit 210 as shown in figure 2, which has the following independent variants:

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- on the second portion of the cold branch, the dihydrogen flow 52 on output from the second expander 216 is supplied to a fifth expander 717, the flow from the fifth expander 717 being supplied to the seventh heat exchanger 707;
 - the first compressor 212 is replaced by a first compressor 712;

- 5 – the second compressor 213 is replaced by a stage of intercooling compression 713, here formed of a series of heat exchangers 719 and compressors 718;
- the dihydrogen flow 52 on output from the stage of intercooling compression 713 being supplied to the fourth heat exchanger 704.

In the embodiment of the device 800 shown in figure 8, the refrigeration circuit 810 is a closed circuit, similar to the refrigeration circuit 210 as shown in figure 2, which has the following variants:

- the maintenance means 815 is positioned on the second portion of the cold branch, between the sixth heat exchanger 806 and the fifth heat exchanger 805;
- the second portion of the cold branch has for source a deviation on the outlet from the third heat exchanger 803 along the hot branch;
- 10 – the dihydrogen flow exiting from the third expander 214 is supplied to the fifth heat exchanger 805;
- the dihydrogen flow exiting from the fifth expander 805 is supplied to the fourth heat exchanger 216;
- 15 – the first compressor 212 is replaced by a series formed of a first compressor 812 and a heat exchanger 813; and
- the second compressor 213 is replaced by a series formed of a second compressor 817 and a heat exchanger 818.

In some embodiments of the device 800, such as that shown in figure 8, the catalytic reactor 20 820 is positioned on a cold branch of the closed refrigeration circuit 810.

In some embodiments of the device 800, such as that shown in figure 8, the closed refrigeration circuit 810 comprises at least one compressor 817 of the dihydrogen refrigerant at ambient temperature and a storage tank 819 for the liquid dihydrogen refrigerant.

In some preferred embodiments, such as those shown in figures 2 to 8 and 10, the closed 25 dihydrogen refrigerant circuit, 210, 310, 410, 510, 610, 710 and/or 810, is configured to maintain an average temperature of the dihydrogen refrigerant between 31 K and 184 K.

As can be understood, the closed circuit 210 comprises a means 215 for maintaining the internal composition of the dihydrogen. Such a maintenance means 215 comprises, for example, at least one catalytic reactor 220 configured to promote a predefined ratio of parahydrogen to 30 orthohydrogen. This ratio is selected so as to be lower or higher than the same ratio in a state of natural equilibrium of a closed circuit 210 not comprising a maintenance means 215. The increase in the relative proportion of parahydrogen in the composition of the dihydrogen improves the performance of the dihydrogen in the heat exchanges taking place within the device 100.

In some particular embodiments 200, as shown in figure 2, the catalytic reactor 220 is 35 positioned on a hot branch of the closed circuit 210.

5 In some particular embodiments 300, as shown in figure 3, the catalytic reactor 320 is positioned on a cold branch of the closed circuit 310.

 In some particular embodiments 400, as shown in figure 4, the maintenance means 415 comprises two catalytic reactors, 420 and 421, positioned on a hot branch of the closed circuit 210. These two catalytic reactors, 420 and 421, are, for example, positioned either side of a heat exchanger with the flow 51 of gas to be liquefied. This heat exchanger is, for example, the fourth heat exchanger 404 in a general series of a pre-cooling section with three heat exchangers, which corresponds to the first heat exchanger of the cooling section.

 In some particular embodiments 500, as shown in figure 5, the catalytic reactor 520 is a reactor referred to as "short" positioned on a hot branch of the closed circuit 510.

10 In some particular embodiments 600, as shown in figure 6, the maintenance means 615 comprises a catalytic reactor 620 and a bypass 616 of the reactor 620, positioned on a hot branch of the closed circuit 610.

 The bypass 616 is, for example, a valve mounted on a pipe for which the inlet is located upstream from the reactor 620 and the outlet is located downstream from the reactor 620. This valve can be flow rate regulated to the flow rate passing through the reactor 620.

15 In some variants, the bypass 616 is associated with a control device, such as an automaton for example, configured to emit activation or de-activation commands to the bypass 616 as a function of activation criteria determined.

 In some embodiments, such as that shown in figure 10, shown in a non-limiting way as a variant of figure 2, the maintenance means 1115 comprises at least one catalytic reactor 1120 integrated into a heat exchanger 204. The catalytic reactor 1120 can be integrated into any heat exchanger, 202, 203, 204, 205, 206, 207, 208 or 209, of the closed circuit 52.

 In some preferred embodiments, such as those shown in figures 2 to 8, the catalytic reactor, 220, 320, 420, 520, 620, 720 and/or 820, is configured to operate according to a temperature between 31 K and 184 K.

25 Any heterogeneous catalyser having a paramagnetic activity, chemically compatible with the dihydrogen and physically compatible with cryogenic temperatures, can be utilised. One example of such a catalyser is the IONEX (Registered Trademark), i.e. a formula containing Fe_2O_3 of the iron oxides family. Another working example is, for example, the OXYSORB (Registered Trademark), i.e. a formula containing CrO_4 . A non exhaustive list of compatible catalysers known from the literature is given below:

- Cr_2O_3 ;
- $\text{Cr}(\text{OH})_3$;
- $\text{Mn}(\text{OH})_4$;
- $\text{Fe}(\text{OH})_4$;
- $\text{Co}(\text{OH})_3$; and

– Ni(OH)_2 .

In some preferred embodiments, the maintenance means, 215, 315, 415, 515, 615, 715 and/or 815, is configured to maintain the proportion of parahydrogen in the internal composition of the dihydrogen refrigerant flow between 27% and 96%.

5 As can be understood, for example, the cooling loop is a double-pressure loop, referred to as a "Claude" loop, and the refrigerant used is hydrogen. The refrigerant fluid 52 is first compressed to 29 bars by a multi-stage compressor 213. The temperature of the fluid 52 on output from the compressor 213 is approximately 171 K (-102°C). The fluid 52 is cooled to 80 K (-193°C) with two heat exchangers, 202 and 203, by exchange with a pre-cooling fluid, such as nitrogen for example.
 10 The fluid 52 next enters into a cooling section and is cooled to 69 K (-204°C) in the first cooling heat exchanger 204. The hydrogen flow 52 passes through a catalytic conversion reactor 220 where the hydrogen reaches an equilibrium composition for the operating temperature considered. In this case, the hydrogen is, for example, composed of 58% parahydrogen and 42% orthohydrogen. The hydrogen is therefore slightly heated between 0.1 K and 0.5 K in steady rate
 15 mode. The refrigerant is then separated, 89% of the total throughput is expanded, by an expander 214, to 18.5 bars and reaches 60 K (-213°C). The flow 52 is then cooled to 51 K (-222°C) in a heat exchanger 206, then expanded with a two-stage expander 216 to 4.5 bars to reach 31.5 K (-241.5°C). From this point, the flow 52 is used as refrigerant in the cooling heat exchangers, 207, 206, 205 and 204. The remaining portion (11%) is cooled to 26 K through four heat exchangers,
 20 205, 206, 207 and 208. This portion is then expanded with an expansion valve 211 to 1.5 bar to reach 22 K. The liquid refrigerant cools the feed flow to 22 K in two biphasic heat exchangers, 209 and 208, and four multi-flow heat exchangers, 207, 206, 205 and 204. The two refrigerant flows, at 4.5 and 1.5 bars, exit from the cooling section at 78 K (-195°C). The low pressure flow is compressed to 4.5 in a first compressor 212. The flow from the first compressor 212 is then mixed
 25 with the medium pressure flow before entering the second compressor 213.

In some preferred embodiments, the closed refrigeration circuit, 210, 310, 410, 510, 610, 710 and/or 810, is configured such that the dihydrogen refrigerant flow 52 has, on input to the catalytic reactor, 220, 320, 420, 520, 620, 720 and/or 820, a temperature essentially equal to the average temperature of the dihydrogen refrigerant 52 in the closed circuit, 210, 310, 410, 510, 610,
 30 710 and/or 810.

In some preferred embodiments, such as those shown in figures 2 to 8 and 10, the device, 200, 300, 400, 500, 600, 700 and/or 800, comprises a circuit 54 for pre-cooling the gas to be liquefied, this pre-cooling circuit comprising at least one heat exchanger, 203, 303, 403, 503, 603, 703 and/or 802, for exchanging heat between a pre-cooling fluid flow and the dihydrogen refrigerant
 35 flow 52.

In some embodiments, the pre-cooling circuit 54 is configured to convey nitrogen having a temperature between 298 K and 80 K. The purpose of such a pre-cooling circuit 54 is to cool the gas 51 to be liquefied and the dihydrogen refrigerant from 90 K to 80 K.

5 In the embodiments of the device 200, 300, 400, 500 and/or 600 shown in figures 2 to 6, the pre-cooling circuit 54 is a closed circuit which comprises:

- a branch referred to as "hot", in which the pre-cooling circuit 54 passes successively through:
 - the first heat exchanger, 201, 301, 401, 501 and/or 601;
 - 10 the second heat exchanger, 202, 302, 402, 502 and/or 602; and
 - an expansion valve 56,
- a branch referred to as "cold", formed of two portions:
 - a first portion, having for source the output from the expansion valve 56, in which the pre-cooling circuit 54 passes successively through:
 - 15 the third heat exchanger, 203, 303, 403, 503 and/or 603;
 - the second heat exchanger, 202, 302, 402, 502 and/or 602;
 - the first heat exchanger, 201, 301, 401, 501 and/or 601;
 - a compressor 57; and
 - a dedicated heat exchanger 58,
 - 20 the pre-cooling fluid on output from the dedicated heat exchanger 58 being supplied to the first heat exchanger, 201, 301, 401, 501 and/or 601, and
 - a second portion, having for source a deviation located at the outlet from the first heat exchanger, 201, 301, 401, 501 and/or 601, in which the pre-cooling circuit 54 passes through an expander 59, the pre-cooling fluid on output from the expander
 - 25 59 being supplied to the second heat exchanger, 202, 302, 402, 502 and/or 602.

In a particular embodiment of the device 700 shown in figure 7, the pre-cooling circuit 54 is similar to the cooling circuit 54 shown in figures 2 to 6, the compressor 57 being formed of a series of compressors. In this embodiment, the flow 54 of refrigerant fluid is utilised in at least one heat exchanger 719 of the intercooling compression stage 713 and in at least one stage 718 of compression at a temperature below -40°C.

30 In a particular embodiment of the device 800 shown in figure 8, the pre-cooling circuit 54 is an open circuit.

As can be understood, for example, the pre-cooling from 300 K (27°C) to 80 K (-193°C) is performed by a closed nitrogen loop. The nitrogen is first compressed from 1 bar to 50 bars by a multi-stage compressor 57. This nitrogen is then cooled to 200 K (-73°C) in a heat exchanger 201. The nitrogen is then separated, 97% of the total throughput is expanded to 1.1 bar in an expander 59 and reaches 81 K (-192°C). This nitrogen returns in the form of coolant in the first pre-cooling heat exchanger 201. The remaining portion (3%) is cooled to 83 K (-190°C). This portion is then partially liquefied by an expansion valve 56, reaching 78 K (-195°C), and operates in the third heat exchanger 203 as main coolant. The remaining cold power of the nitrogen is used in the pre-cooling heat exchangers, 202 and 201.

Figure 10 shows a particular series of steps of the method 1000 that is the subject of the present invention. This method 1000 for liquefying a gas comprises:

- a step 1005 of conveying gas to be liquefied, the step comprising at least one step 1010 of exchanging heat between the gas to be liquefied and a refrigerant flow comprising at least dihydrogen refrigerant;
- a step 1015 of conveying, in a closed refrigeration circuit, the refrigerant flow, the conveying step comprising a step 1020 of maintaining an internal composition of the dihydrogen refrigerant at a ratio of parahydrogen to orthohydrogen that is lower or higher than the ratio corresponding to a natural equilibrium composition in the closed refrigerant flow circuit, this maintenance means comprising a catalytic reaction step 1025 to convert some of the orthohydrogen from the dihydrogen refrigerant into parahydrogen or vice versa.

Embodiment of the steps of this method 1000 are described with reference to figures 2 to 8 and 10.

As can be understood, a particular composition of the dihydrogen refrigerant that is the subject of the present invention comprises 58% parahydrogen and 42% orthohydrogen, this composition not being the natural equilibrium composition. This is a compromise to obtain the best match of the thermal properties of the gas, both during its compression and in its role as coolant.

In fact, the main effect of the increase in the parahydrogen content is to induce an increase in the thermal calorific capacity of the hydrogen. The result of this is to increase the energy to be supplied or dissipated for modifying its temperature. In compression, this has the effect of reducing the temperature increase between the inlet and the outlet, the density of the hydrogen thus declining accordingly. However, the denser a gas, the easier it is to compress it. The compression power of the hydrogen therefore reduces correspondingly as the latter is compressed in a form converted most into parahydrogen.

As can be understood, the present invention provides high operating performance under the following operating conditions, with regard to the device 200 shown in figure 2:

Table 1

Parameters	Lower limit	Upper limit
Pre-cooling temperature (K/°C)	60 / -213	150 / -123
Compression inlet temperature (K/°C)	31 / -242	250 / -23
Parahydrogen fraction (%)	27%	96%
Catalysis temperature (K/°C)	31 / -232	184 / -89
Average coolant temperature (K)	31 / -232	184 / -89

Minimum operating time (j)	30	-
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In the embodiment of the device 300 shown in figure 3, the catalytic reactor 320 is positioned on a return branch of the cooling loop, which shifts the equilibrium of the cycle as a function of the temperature associated with it. An advantageous position of the reactor 320 is located between the fifth heat exchanger 305 and the sixth heat exchanger 306. In such an embodiment, the catalysis temperature is 54 K (-219°C) (for a composition of 74% p-H₂ and 26% o-H₂).

In another embodiment of the device 400, as shown in figure 4, the catalytic conversion is performed in several catalytic reactors, 420 and 421, configured at different temperatures and thus aimed at a conversion by steps of the coolant hydrogen. This is of interest insofar as the heat generated during the conversion increases inversely with the temperature. In such an embodiment, a first conversion is performed at 80 K (-193°C), bringing the hydrogen to a composition of 52% p-H₂, and then a second conversion is performed at 69 K (-204°C), bringing the hydrogen to the target composition of 58% p-H₂.

In another embodiment of the device 500, as shown in figure 5, a partial conversion to a temperature other than the target temperature associated with the target equilibrium composition is performed. This is realisable insofar as the reactor 520 is sized such that the passage time or the reactivity of the catalyser do not make it possible to reach thermodynamic equilibrium. For example, the reactor 520 is placed at a catalysis temperature of 56 K (-217°C), but the reduction in the length of the reactor 520 makes it possible to reach the target composition of 58% p-H₂ instead of the equilibrium composition of 70% p-H₂ associated with the temperature of 56 K (-217°C).

In another embodiment of the device 600, as shown in figure 6, the target composition can be selected using a partial bypass device of the reactor 620. Thus the final composition corresponds to the average of the output compositions of the reactor 620 and bypass 616 weighted by the respective flow rates passing through them.

In another embodiment of the device 700, as shown in figure 7, the present invention is applied in the context of a cryogenic compression referred to as with intermediate cooling (referred to as an "intercooler"), i.e. cooling the cooling fluid between each stage.

In another embodiment of the device 800, as shown in figure 8, the placement of the catalytic reactor 820 is configured such that the compression is performed at ambient temperature. If the average temperature of the dihydrogen refrigerant remains below 184 K (-89°C), which is, for example, the case if a buffer storage for liquid hydrogen is used after the valve 53. Therefore, in this embodiment, the increase in the parahydrogen content makes it possible to reduce the natural conversion in the liquid buffer storage, making it possible to reduce and shift a part of the associated losses to a location of the method less sensitive to heat emissions.

- 5 The present invention is particularly suited to the case of liquid hydrogen production greater than five tonnes a day, because the reduced investment requirement and the stability of the method in operation enable savings in the final cost of the liquefaction of hydrogen.

CLAIMS

1. Device (200, 300, 400, 500, 600, 700, 800, 1100) for liquefying a gas (51), which device is characterised in that it comprises:

- a circuit (55) for conveying gas to be liquefied, the circuit comprising at least one heat exchanger (204, 304, 404, 504, 604, 704, 804) for exchanging heat between the gas (51) to be liquefied and a refrigerant flow (52) comprising at least dihydrogen refrigerant;

- 5 – a closed refrigeration circuit (210, 310, 410, 510, 610, 710, 810) configured to convey the refrigerant flow,

the closed refrigeration circuit comprising a means (215, 315, 415, 515, 615, 715, 815, 1115) for maintaining an internal composition of the dihydrogen refrigerant at a ratio of parahydrogen to orthohydrogen that is lower or higher than the ratio corresponding to a natural equilibrium composition in the closed refrigerant flow circuit, this maintenance means comprising a catalytic reactor (220, 320, 420, 520, 620, 720, 820, 1120) configured to convert some of the orthohydrogen from the dihydrogen refrigerant flow into parahydrogen or vice versa.

2. Device (200, 400, 500, 600, 700, 800, 1100) according to claim 1, wherein the closed refrigeration circuit (210, 310, 410, 510, 610, 710, 810) is configured such that the dihydrogen refrigerant has, on input to the catalytic reactor (220, 320, 420, 520, 620, 720, 820), a temperature essentially equal to the average temperature of the dihydrogen refrigerant in the closed circuit.

3. Device (200, 400, 500, 600, 1100) according to one of claims 1 or 2, wherein the catalytic reactor (220, 420, 520, 620) is positioned on a hot branch of the closed refrigeration circuit (210, 410, 510, 610).

4. Device (200, 300, 400, 500, 600, 700, 800, 1100) according to one of claims 1 to 3, wherein the catalytic reactor (220, 320, 420, 520, 620, 720, 820) is configured to operate according to a temperature between 31 K and 184 K.

5. Device (200, 300, 400, 500, 600, 700, 800, 1100) according to one of claims 1 to 4, wherein the maintenance means (215, 315, 415, 515, 615, 715, 815) is configured to maintain the proportion of parahydrogen in the internal composition of the dihydrogen refrigerant between 27% and 96%.

6. Device (600) according to one of claims 1 to 5, wherein the maintenance means (615) comprises a bypass (616) of the catalytic reactor configured to operate a predefined throughput ratio between the flow passing through the reactor (620) and the flow passing through the bypass.

7. Device (200, 300, 400, 500, 600, 700, 800, 1100) according to one of claims 1 to 6, wherein the closed dihydrogen refrigerant circuit (210, 310, 410, 510, 610, 710, 810) is configured to maintain an average temperature of the dihydrogen refrigerant between 31 K and 184 K.

8. Device (200, 300, 400, 500, 600, 700, 800, 1100) according to one of claims 1 to 7, which comprises a circuit (54) for pre-cooling the gas to be liquefied, this pre-cooling circuit comprising a heat exchanger (203, 303, 403, 503, 603, 703, 802) for exchanging heat between a pre-cooling fluid flow and the dihydrogen refrigerant flow (52).

9. Device (200, 300, 400, 500, 600, 700, 800, 1100) according to one of claims 1 to 8, wherein the gas to be liquefied is a flow comprised essentially of dihydrogen.

10. Device (1100) according to one of claims 1 to 9, wherein at least one catalytic reactor (1120) is integrated into a heat exchanger (204).

11. Device (700) according to one of claims 1 to 10, wherein the closed refrigeration circuit (710) comprises a stage (713) of intercooling compression and at least one stage (718) of compression at a temperature below -40°C for the dihydrogen refrigerant.

12. Device (800) according to one of claims 1 to 11, wherein the catalytic reactor (820) is positioned on a cold branch of the closed refrigeration circuit (810).

13. Device (800) according to one of claims 1 to 12, wherein the closed refrigeration circuit (810) comprises at least one compressor (817) of the dihydrogen refrigerant at ambient temperature and a storage tank (819) for the liquid dihydrogen refrigerant.

14. Device (200, 300, 400, 500, 600, 700, 800, 1100) according to one of claims 1 to 13, wherein the catalytic reactor (220, 320, 420, 520, 620, 720, 820) utilises a catalyser comprising a member of the iron oxides family, preferably Fe_2O_3 .

15. Method (1000) for liquefying a gas, characterised in that it comprises:

- a step (1005) of conveying gas to be liquefied, the step comprising at least one step (1010) of exchanging heat between the gas to be liquefied and a refrigerant flow comprising at least dihydrogen refrigerant;

- a step (1015) of conveying, in a closed refrigeration circuit, the refrigerant flow, the conveying step comprising a step (1020) of maintaining an internal composition of the dihydrogen refrigerant at a ratio of parahydrogen to orthohydrogen that is lower or higher than the ratio corresponding to a natural equilibrium composition in the closed refrigerant flow circuit, this

maintenance means comprising a catalytic reaction step (1025) to convert some of the orthohydrogen from the dihydrogen refrigerant into parahydrogen or vice versa.