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(54) **LIQUID HYDROGEN PRODUCTION DEVICE**

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(57) **ABSTRACT**

A device (HS) is provided with a refrigeration cycle unit (R) and a liquid hydrogen generation unit (P) for generating liquid hydrogen by cooling high-pressure raw material hydrogen by means of the refrigeration cycle unit (R) and by adiabatically expanding said raw material hydrogen by means of a Joule-Thomson valve (**12**). A first and second heat exchanger (E**1**, E**2**) are disposed along the refrigeration cycle unit (R) and the liquid hydrogen generation unit (P). The device (HS) is provided with a mechanism for generating liquid hydrogen by re-liquefying the boil-off gas generated in a liquid hydrogen storage tank. The boil-off gas is introduced into a hydrogen circulation path (**1**) at a section at which circulating hydrogen having an extremely low temperature flows, and the excessive circulating hydrogen generated therefrom is discharged to a raw material hydrogen path (**11**) from a section at which the circulating hydrogen is at room temperature.

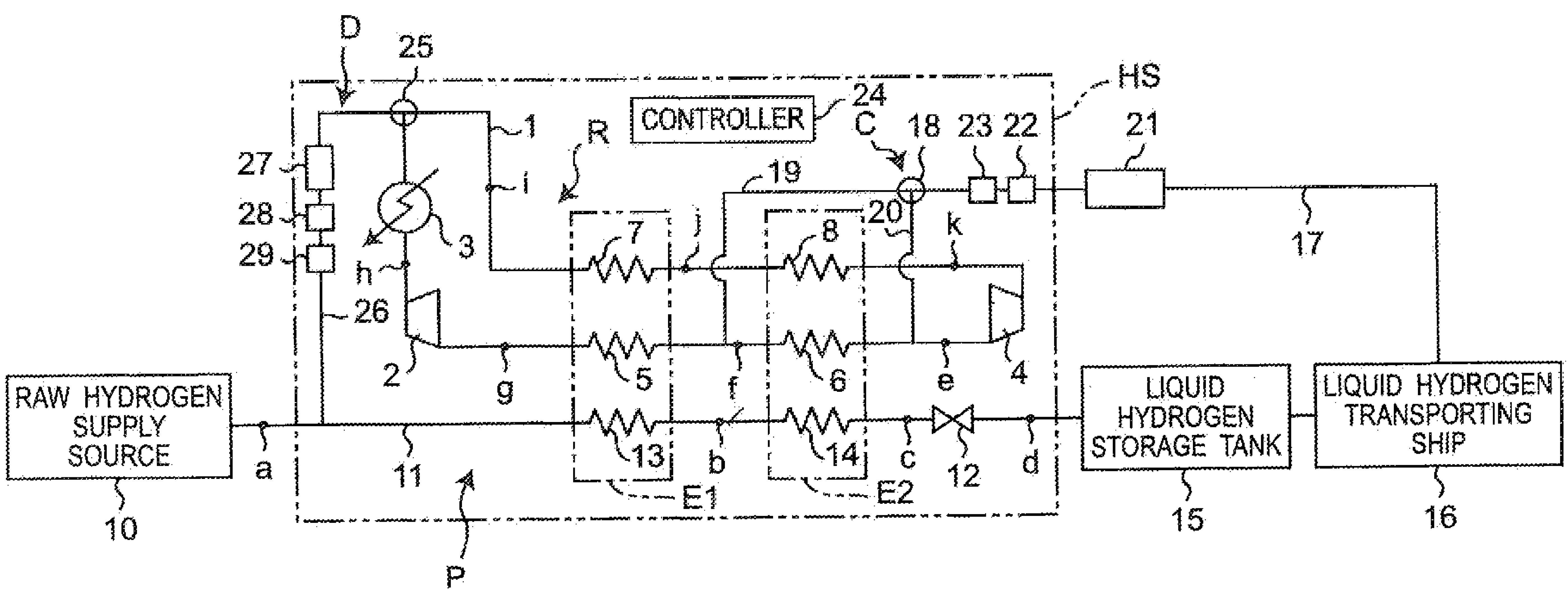
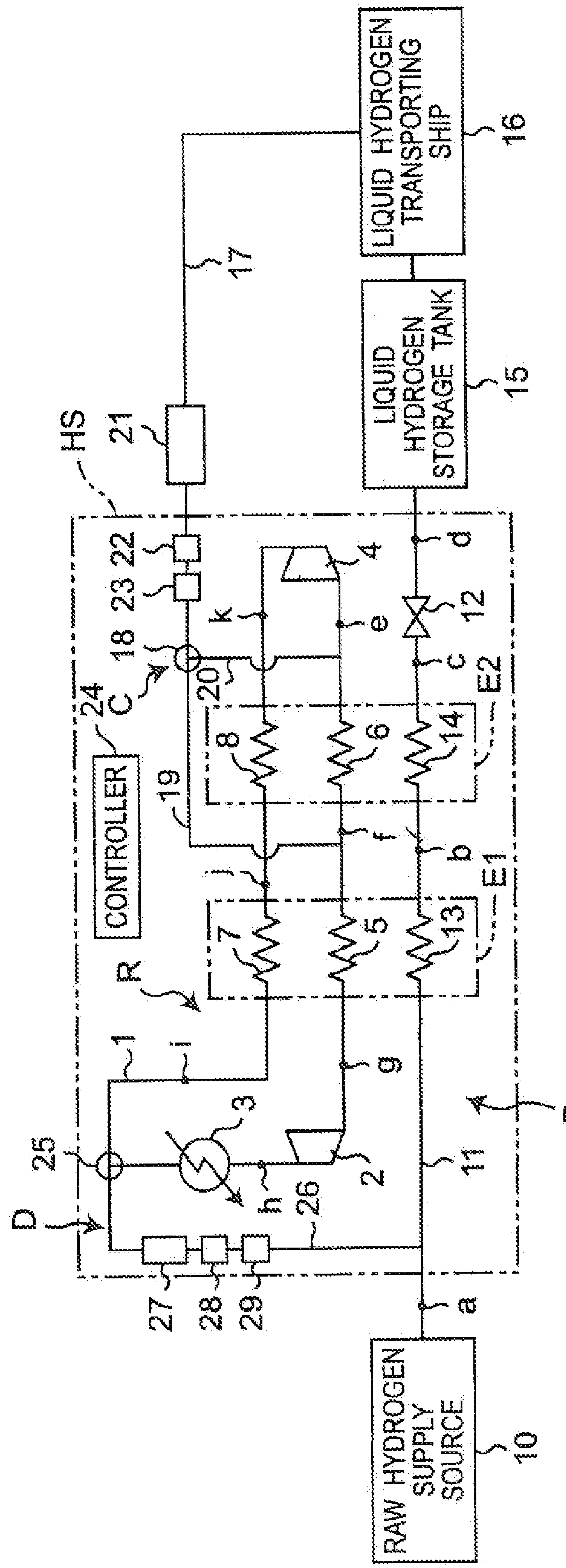


Fig. 1


RAW HYDROGEN SUPPLY SOURCE
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LIQUID HYDROGEN STORAGE TANK
15
LIQUID HYDROGEN TRANSPORTING SHIP
16
CONTROLLER
24
HS
C
D
R
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LIQUID HYDROGEN PRODUCTION DEVICE

TECHNICAL FIELD

[0001] The present invention relates to an apparatus for producing liquid hydrogen including a mechanism for treating boil-off gas generated in a liquid hydrogen vessel of a liquid hydrogen transporting ship or the like, the mechanism being adapted to re-liquefy the boil-off gas for its reuse.

BACKGROUND ART

[0002] Hydrogen is conventionally and widely used as a raw material, a reduction agent or the like in various technical fields such as chemical industries, petroleum refinery industries, iron manufacturing industries or the like. Meanwhile, policy to reduce carbon-dioxide emissions is recently adopted on a global scale while the price of fossil fuel such as crude oil is continuously running up. Thus, in recent years, it is intended to utilize hydrogen as fuel or energy sources in various technical fields. In particular, it is intended to utilize hydrogen as fuel for engines of automobiles or turbines of electricity generators. Hydrogen is conventionally produced by means of a steam reforming process of hydrocarbons, an electrolysis process of water or the like. Meanwhile, it is also possible to produce hydrogen by means of a hydrogen producing system which produces hydrogen using low-grade coal such as lignite or the like as one main raw material.

[0003] Meanwhile, when hydrogen is produced, for example by using low-grade coal as one main raw material, the hydrogen producing system is generally established near a producing area of the low-grade coal. On the other hand, a market area of hydrogen mainly exists in a populated area such as an urban area or the like, which is generally distant from the producing area of the low-grade coal. Accordingly, it is necessary to transport hydrogen produced in the hydrogen producing system to the market area of hydrogen.

[0004] In general, when hydrogen is transported to the market area across a sea or ocean, hydrogen produced in the hydrogen producing system is cooled so as to be liquefied by a hydrogen liquefier, and stored in a liquid hydrogen storage tank as disclosed, for example in JP 2005-241232 A. Then, the liquid hydrogen is conveniently transported to the market area. Thus, in order to transport the liquid hydrogen across the sea or ocean, in general, a liquid hydrogen transporting ship is used, which is equipped with a liquid hydrogen vessel for storing the liquid hydrogen while keeping it at very low temperature.

SUMMARY OF INVENTION

Problems to be Solved by the Invention

[0005] When the liquid hydrogen is intermittently transported to the market area of hydrogen by means of the liquid hydrogen transporting ship, at first, the liquid hydrogen stored in the liquid hydrogen storage tank is supplied to the liquid hydrogen vessel of the liquid hydrogen transporting ship, which is harboring in a port (referred to as "shipping port" hereinafter) near the place where the hydrogen liquefier or the liquid hydrogen storage tank is located. Then, the liquid hydrogen transporting ship travels across the sea or ocean and reaches another port (referred to as "landing port" hereinafter) near the market area of hydrogen. Thus, the liquid hydrogen stored in the liquid hydrogen vessel of the liquid hydrogen transporting ship is supplied to another liquid hydrogen storage tank located near the landing port. After that, the liquid hydrogen transporting ship in the landing port, whose liquid hydrogen vessel still holds a suitable amount (for example, a few percent in volume with respect to the volume of the liquid hydrogen vessel) of liquid hydrogen for keeping the liquid hydrogen vessel in a cold state, returns to the shipping port.

[0006] Thus, in the shipping port again, the liquid hydrogen stored in the liquid hydrogen storage tank near the shipping port is supplied to the liquid hydrogen vessel of the liquid hydrogen transporting ship. On that occasion, the temperature of the liquid hydrogen vessel of the liquid hydrogen transporting ship has been raised because heat outside of the liquid hydrogen vessel was transmitted to the liquid hydrogen vessel when the liquid hydrogen transporting ship was traveling from the landing port to the shipping port or when the liquid hydrogen transporting ship was harboring in the shipping port. In particular, the temperature in the upper portion of the liquid hydrogen vessel has become higher than the saturation temperature of the liquid hydrogen. In consequence, when the liquid hydrogen in the liquid hydrogen storage tank is supplied to the liquid hydrogen vessel, the supplied liquid hydrogen is partially vaporized resulting from the difference between the temperature of the liquid hydrogen vessel and the temperature of the supplied liquid hydrogen so that boil-off gas of large amounts is generated. Thus, it is necessary to treat the boil-off gas of large amounts in a short time because the liquid hydrogen transporting ship is merely harboring within a short time of one day or a few days.

[0007] In order to address this problem, it is probable to use such a solution to mix the generated boil-off gas of large amounts with hydrogen as a raw material supplied from the hydrogen producing system to the hydrogen liquefier, and re-liquefies it by means of the hydrogen liquefier for its reuse. However, if the boil-off gas, whose temperature is very low, is simply used as a raw material of the hydrogen liquefier, there may be caused such a problem that it causes a trouble of the hydrogen liquefier, which is designed on the assumption that hydrogen as the raw material is supplied at ordinary temperature. Thus, if the boil-off gas is heated to ordinary temperature and then mixed with hydrogen as the raw material, it is possible to dissolve the above-mentioned trouble. However, according to this solution, the boil-off gas in the state of very low temperature is once heated to ordinary temperature, and then cooled to the state of extremely low temperature again by the hydrogen liquefier. Thus, this solution is very unreasonable in the view point of energy efficiency because the cold energy of the boil-off gas is wasted. Similar problems may be caused as for boil-off gas generated in any liquid hydrogen reservoir equipped in a means for transporting the liquid hydrogen other than the liquid hydrogen transporting ship.

[0008] The present invention, which has been made to solve the conventional problem described above, has an object to provide a means which can effectively utilize and re-liquefy boil-off gas without wasting its cold energy to reproduce liquid hydrogen, the boil-off gas being generated in a liquid hydrogen reservoir of a transporting means for transporting liquid hydrogen, such as a liquid hydrogen vessel of a liquid hydrogen transporting ship or the like.

Means for Solving the Problems

[0009] An apparatus for producing liquid hydrogen according to the present invention, which has been made to achieve the above-mentioned object, includes a refrigeration cycle unit in which circulating hydrogen flows as a refrigerant, and a liquid hydrogen producing unit for producing the liquid hydrogen from gaseous hydrogen. The apparatus is characterized in that it further includes a boil-off gas supplying unit for supplying boil-off gas generated in a liquid hydrogen reservoir to the refrigeration cycle unit through a predetermined inlet portion in the refrigeration cycle unit, and a circulating hydrogen discharge unit for discharging excessive circulating hydrogen resulting from the boil-off gas supplied to the refrigeration cycle unit by means of the boil-off gas supplying unit, to the liquid hydrogen producing unit through a predetermined outlet portion in the refrigeration cycle unit.

[0010] According to an embodiment of the present invention, the refrigeration cycle unit includes, a compressor for compressing the circulating hydrogen, an expander for expanding the circulating hydrogen, and at least one heat exchanger interposed between the compressor and the expander, the heat exchanger including a low-temperature heat exchanging element located at an upstream side of the compressor and a high-temperature heat exchanging element located at a downstream side of the compressor. Meanwhile, the liquid hydrogen producing unit includes, a raw hydrogen passage through which the gaseous hydrogen supplied from a raw hydrogen source flows, an expansion valve equipped at a downstream side of the raw hydrogen passage, for expanding the gaseous hydrogen to produce the liquid hydrogen, and at least one gaseous hydrogen cooler for cooling the gaseous hydrogen by heat exchange with the at least one heat exchanger of the refrigeration cycle unit.

[0011] In regard to this, the inlet portion in the refrigeration cycle unit is disposed at a position located downstream of the expander and upstream of the compressor. Meanwhile, the outlet portion in the refrigeration cycle unit is disposed at a position located between the first low-temperature heat exchanging element in an upstream direction from the compressor and the first high-temperature heat exchanging element in a downstream direction from the compressor.

[0012] In the apparatus for producing the liquid hydrogen according to the present invention, it is preferable that the inlet portion in the refrigeration cycle unit is composed of a plurality of inlet elements disposed depending on the difference between the temperature of the circulating hydrogen in the refrigeration cycle unit and the temperature of the boil-off gas generated in the liquid hydrogen reservoir. Meanwhile, it is preferable that the outlet portion in the refrigeration cycle unit is disposed between the compressor and the first high-temperature heat exchanging element in a downstream direction from the compressor.

[0013] In the apparatus for producing the liquid hydrogen according to the present invention, it is preferable that the expander is an expansion turbine while the expansion valve is a Joule-Thomson valve. The liquid hydrogen reservoir of the apparatus for producing the liquid hydrogen according to the present invention may include, for example a liquid hydrogen vessel of a liquid hydrogen transporting ship.

Advantages of the Invention

[0014] According to the present invention, the boil-off gas in the state of very low temperature, which is discharged, for example from the liquid hydrogen vessel of the liquid hydrogen transporting ship, is supplied to the hydrogen circulating passage of the refrigeration cycle unit through the inlet portion where the circulating hydrogen in the state of very low temperature flows. Because the difference between the temperature of the boil-off gas and the temperature of the circulating hydrogen is relatively small at the inlet portion, any particular trouble is not caused in the apparatus for producing the liquid hydrogen when the boil-off gas in the state of very low temperature is supplied to the refrigeration cycle unit through the inlet portion. Moreover, cold energy of the boil-off gas in the state of very low temperature is not wasted.

[0015] On the other hand, the excessive circulating hydrogen resulting from the boil-off gas supplied to the refrigeration cycle unit is discharged from a position in the hydrogen circulating passage where the circulating hydrogen flows at nearly ordinary temperature, to a position in the raw hydrogen passage where the raw hydrogen flows at nearly ordinary temperature. Because the difference between the temperature of the circulating hydrogen and the temperature of the raw hydrogen is relatively small in the latter point, any particular trouble is not caused in the apparatus for producing the liquid hydrogen when the excessive circulating hydrogen is supplied to the raw hydrogen passage. Moreover, the amount of the circulating hydrogen in the refrigeration cycle unit is maintained at an adequate level because the excessive circulating hydrogen is preferably discharged.

[0016] Thus, the excessive circulating hydrogen which is discharged to the raw hydrogen passage is re-liquefied in the liquid hydrogen producing unit to become the liquid hydrogen. When the functions of the apparatus for producing the liquid hydrogen are viewed as a whole, the boil-off gas in the state of very low temperature is supplied to the apparatus for producing the liquid hydrogen while the liquid hydrogen, whose amount corresponds to the amount of the supplied boil-off gas, is produced. Therefore, according to the present invention, the boil-off gas in the state of very low temperature is supplied to the apparatus for producing the liquid hydrogen without causing any trouble in any member of the apparatus for producing the liquid hydrogen so that the liquid hydrogen, whose amount corresponds to the amount of the supplied boil-off gas, is produced. In other words, the boil-off gas in the state of very low temperature generated in the liquid hydrogen reservoir is re-liquefied to become the liquid hydrogen for its reuse without wasting the cold energy of the boil-off gas and with effectively utilizing the cold energy.

BRIEF DESCRIPTION OF DRAWINGS

[0017] FIG. **1** is a schematic view showing a system configuration of a liquid hydrogen producing apparatus according to the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0018] An embodiment of the present invention will be described in detail hereinafter, with reference to the accompanying drawings.

[0019] As shown in FIG. **1**, a liquid hydrogen producing apparatus HS according to an embodiment of the present invention is equipped with a refrigeration cycle unit R in which hydrogen (referred to as "circulating hydrogen" hereinafter) circulates as a refrigerant, and a liquid hydrogen producing unit P for producing liquid hydrogen by cooling gaseous hydrogen (referred to as "raw hydrogen" hereinafter) as a raw material by means of the refrigeration cycle unit R and then adiabatically expanding the raw hydrogen.

[0020] The refrigeration cycle unit R is equipped with a hydrogen circulating passage **1** of a circular configuration, through which the circulating hydrogen flows in circle. The circulating hydrogen flows in circle clockwise in the hydrogen circulating passage **1** in view of the positional relationship shown in FIG. **1**. Hereinafter, for the sake of convenience, the upstream side and the downstream side with respect to the direction, along which the circulating hydrogen flows, are merely referred to as "upstream" and "downstream", respectively. The hydrogen circulating passage **1** is equipped with a compressor **2**, a circulating hydrogen cooler **3** located at the downstream side of the compressor **2** and an expansion turbine **4** located at the downstream side of the circulating hydrogen cooler **3**, each of which is interposed in the hydrogen circulating passage **1**.

[0021] The compressor **2**, which may be, for example a compression machine driven by an electric motor, adiabatically compresses the circulating hydrogen in the state of ordinary pressure (for example, 0.1 MPaA) and ordinary temperature (for example, 300K) so as to make the circulating hydrogen become such a state of high pressure (for example, 2 MPaA) and high temperature (for example, 780K). The circulating hydrogen cooler **3**, which may be, for example a heat exchanger using cooling water at low temperature as a cooling medium, cools the circulating hydrogen at high pressure and high temperature so as to make the circulating hydrogen become such a state of ordinary temperature while maintaining its high pressure. Thus, the circulating hydrogen at high pressure and ordinary temperature is cooled before reaching the expansion turbine **4** by first and second heat exchangers E**1** and E**2** as described later in detail so that the circulating hydrogen reaches such a state of very low temperature (for example, 40K) while maintaining its pressure. The expansion turbine **4**, which may be a turbine for transforming pressure energy or kinetic energy of a gas at high pressure into mechanical energy and then outputs the mechanical energy outward, is driven by the circulating hydrogen at high pressure and very low temperature while it lowers the pressure and temperature of the circulating hydrogen to liquefy at least a part of the circulating hydrogen so that the circulating hydrogen reaches such a state of ordinary pressure and extremely low temperature (for example, 20K). Alternatively, instead of the expansion turbine **4**, it is possible to use an expansion machine such as a Joule-Thomson valve or the like, which adiabatically expands the circulating hydrogen.

[0022] In addition, the hydrogen circulating passage **1** is equipped with first and second low-temperature heat exchanging elements **5** and **6**, each of which is disposed at a respective position located downstream of the expansion turbine **4** and upstream of the compressor **2**. Moreover, the hydrogen circulating passage **1** is equipped with first and second high-temperature heat exchanging elements **7** and **8**, each of which is disposed at a respective position located downstream of the circulating hydrogen cooler **3** and upstream of the expansion turbine **4**. The first low-temperature heat exchanging element **5** and the first high-temperature heat exchanging element **7** are disposed at mutually corresponding positions so as to mutually exchange heat thereof. The second low-temperature heat exchanging element **6** and the second high-temperature heat exchanging element **8** are disposed at mutually corresponding positions so as to mutually exchange heat thereof. Each of the first low-temperature heat exchanging element **5** and the first high-temperature heat exchanging element **7** is a component of the first heat exchanger E**1** described later in detail, while each of the second low-temperature heat exchanging element **6** and the second high-temperature heat exchanging element **8** is a component of the second heat exchanger E**2** described later in detail.

[0023] The liquid hydrogen producing unit P is equipped with a raw hydrogen passage **11**, through which the raw hydrogen in the state of high pressure (for example, 2 MPaA) and ordinary temperature supplied from a raw hydrogen supply source **10** flows. A Joule-Thomson valve **12** is connected to the downstream end of the raw hydrogen passage **11** with respect to the direction (rightward in view of the positional relationship shown in FIG. **1**) along which the raw hydrogen flows. In addition, a first raw hydrogen cooling element **13** and a second raw hydrogen cooling element **14** are interposed in the raw hydrogen passage **11**, in turn from the upstream side to the downstream side with respect to the direction along which the raw hydrogen flows. The first and second raw hydrogen cooling elements **13** and **14** cool the raw hydrogen in the state of high pressure and ordinary temperature so that the raw hydrogen reaches such a state of very low-temperature (for example, 40K) while approximately maintaining its pressure. The Joule-Thomson valve **12** adiabatically expands the raw hydrogen in the state of high pressure and very low-temperature so as to lower the pressure and temperature of the raw hydrogen. In consequence, at least a part of the raw hydrogen is liquefied so that liquid hydrogen is produced. Alternatively, in order to liquefy the raw hydrogen, an expansion valve other than the Joule-Thomson valve may be used. The first raw hydrogen cooling element **13** may be a component of the first heat exchanger E**1** described later in detail while the second raw hydrogen cooling element **14** may be a component of the second heat exchanger E**2** described later in detail.

[0024] In the liquid hydrogen producing apparatus HS, the first and second heat exchangers E**1** and E**2** are arranged across the refrigeration cycle unit R and the liquid hydrogen producing unit P, the first heat exchanger E**1** including the first low-temperature heat exchanging element **5**, the first high-temperature heat exchanging element **7** and the first raw hydrogen cooling element **13**, and the second heat exchanger E**2** including the second low-temperature heat exchanging element **6**, the second high-temperature heat exchanging element **8** and the second raw hydrogen cooling element **14**. In each of the first and second heat exchangers E**1** and E**2**, the circulating hydrogen flowing through the hydrogen circulating passage **1** at the position downstream of the expansion turbine **4** and upstream of the compressor **2**, cools the circulating hydrogen flowing through the hydrogen circulating passage **1** at the position downstream of the circulating hydrogen cooler **3** and upstream of the expansion turbine **4**, and further cools the raw hydrogen flowing through the raw hydrogen passage **11**.

[0025] In the apparatus according to the embodiment shown in FIG. **1**, two heat exchangers E**1** and E**2** are arranged across the refrigeration cycle unit R and the liquid hydrogen producing unit P. However, the number of the heat exchangers to be equipped is not limited two, and therefore it is possible to use three or more heat exchangers (for example, three, four, five . . .). In other words, the number of the heat exchangers to be equipped may be preferably determined depending on the heat transfer area of each heat exchanger and other heat transfer properties of each heat exchanger.

[0026] Hereinafter, it will be described how the thermodynamic states of the circulating hydrogen or raw hydrogen flowing in the refrigeration cycle unit R or liquid hydrogen producing unit P may be changed. At first, the state changes of the circulating hydrogen flowing from the expansion turbine **4** to the compressor **2** through the hydrogen circulating passage **1** will be described. The circulating hydrogen in the state of ordinary pressure (for example, 0.1 MPaA) and extremely low temperature (for example, 20K), which has flowed away from the expansion turbine **4** and has been at least partially liquefied, cools the circulating hydrogen flowing through the second high-temperature heat exchanging element **8** as well as the raw hydrogen flowing through the second raw hydrogen cooling element **14** when it flows through the second low-temperature heat exchanging element **6**. In consequence, the temperature of the circulating hydrogen in the state of ordinary pressure, which has flowed away from the second low-temperature heat exchanging element **6** (second heat exchanger E**2**) has been raised to a slightly higher temperature (for example, 80K). On that occasion, the liquefied part in the circulating hydrogen is vaporized when it flows through the second low-temperature heat exchanging element **6**.

[0027] The circulating hydrogen, which has flowed away from the second low-temperature heat exchanging element **6** (second heat exchanger E**2**), cools the circulating hydrogen flowing through the first high-temperature heat exchanging element **7** as well as the raw hydrogen flowing through the first raw hydrogen cooling element **13** when it flows through the first low-temperature heat exchanging element **5**. In consequence, the temperature of the circulating hydrogen in the state of ordinary pressure, which has flowed away from the first low-temperature heat exchanging element **5** (first heat exchanger E**1**) has been raised to ordinary temperature (for example, 300K). Then, the circulating hydrogen in the state of ordinary pressure and ordinary temperature flows into the compressor **2**. Thus, the circulating hydrogen is adiabatically compressed by the compressor **2** so that it becomes such a state of high pressure (for example, 2 MPaA) and high temperature (for example, 780K).

[0028] Next, the state changes of the circulating hydrogen flowing from the compressor **2** to the expansion turbine **4** through the hydrogen circulating passage **1** will be described. The gaseous circulating hydrogen in the state of high pressure and high temperature, which has flowed away from the compressor **2**, is cooled at first by the circulation hydrogen cooler **3** so as to reach such a state of ordinary temperature (for example, 300K) and high pressure. Then, the circulating hydrogen in the state of high pressure and ordinary temperature is cooled by the circulating hydrogen flowing through the first low-temperature heat exchanging element **5** so as to reach such a state of very low-temperature (for example, 80K) when it flows through the first high-temperature heat exchanging element **7**. The circulating hydrogen in the state of high pressure and very low temperature, which has flowed away from the first high-temperature heat exchanging element **7** (first heat exchanger E**1**) is cooled by the circulating hydrogen flowing through the second low-temperature heat exchanging element **6** so as to reach such a state of further lower-temperature (for example, 40K) when it flows through the second high-temperature heat exchanging element **8**. Then, the circulating hydrogen in the state of high pressure and very low temperature flows into the expansion turbine **4**. Thus, the circulating hydrogen is expanded by the expansion turbine **4** so as to become such a state of ordinary pressure (for example, 0.1 MPaA) and extremely low temperature (for example, 20K) so that the circulating hydrogen is at least partially liquefied.

[0029] Moreover, the state changes of the raw hydrogen flowing from the raw hydrogen supply source **10** to the Joule-Thomson valve **12** through the raw hydrogen passage **11** will be described. The raw hydrogen in the state of high pressure (for example, 2 MPaA) and ordinary temperature (for example, 300K) supplied by the raw hydrogen supply source **10** is cooled by the circulating hydrogen flowing through the first low-temperature heat exchanging element **5** so as to become such a state of very low temperature (for example, 80K) when it flows through the first raw hydrogen cooling element **13**. The raw hydrogen in the state of high pressure and very low temperature, which has flowed away from the first raw hydrogen cooling element **13** (first heat exchanger E**1**) is cooled by the circulating hydrogen flowing through the second low-temperature heat exchanging element **6** so as to reach such a state of further lower-temperature (for example, 40K) when it flows through the second raw hydrogen cooling element **14**.

[0030] Then, the raw hydrogen in the state of high pressure and very low temperature is expanded by means of the Joule-Thomson expansion when it passes through the Joule-Thomson valve **12** so as to become such a state of ordinary pressure (for example, 0.1 MPaA) and extremely low temperature (for example, 20K) so that the raw hydrogen is at least partially liquefied. The liquefied raw hydrogen, namely the liquid hydrogen as a product of the liquid hydrogen producing apparatus HS, is stored in a liquid hydrogen storage tank **15**. The liquid hydrogen stored in the liquid hydrogen storage tank **15** is conveniently supplied to a liquid hydrogen vessel of a liquid hydrogen transporting ship **16** which is harboring in a port (shipping port) near the area where the liquid hydrogen producing apparatus HS is located.

[0031] Table 1 collectively shows thermodynamic states of the circulating hydrogen or raw hydrogen at respective positions in the refrigeration cycle unit R or the liquid hydrogen producing unit P, the positions being indicated by the reference symbols a-k in FIG. **1**. In Table 1, the symbol “G” denotes a gas state while the symbol “L” denotes a liquid state.

TABLE 1

Thermodynamic states of circulating hydrogen or raw hydrogen

Position	a	b	c	d	e	f	g	h	i	j	k
State	G	G	G	L	L	G	G	G	G	G	G
Temp. [K]	300	80	40	20	20	80	300	780	300	80	40
Pres. [MPaA]	2.0	2.0	2.0	0.1	0.1	0.1	0.1	2.0	2.0	2.0	2.0

[0032] The liquid hydrogen producing apparatus HS according to the present invention is further equipped with a boil-off gas treating mechanism for re-liquefying boil-off gas, which is generated in a liquid hydrogen vessel (not-shown) of the liquid hydrogen transporting ship **16** harboring in the port (shipping port) near the area where the liquid hydrogen producing apparatus HS is located and which is supplied to the boil-off gas treating mechanism, so as to produce the liquid hydrogen. At first, fundamental structure and function of the boil-off gas treating mechanism will be described hereinafter. In short, in the boil-off gas treating mechanism of the liquid hydrogen producing apparatus HS according to the present invention, the boil-off gas in the state of low temperature is supplied to a portion in the hydrogen circulating passage **1** of the refrigeration cycle unit R where the circulating hydrogen in the state of low temperature flows. Meanwhile, the excessive circulating hydrogen resulting from the supply of the boil-off gas is discharged from a portion in the hydrogen circulating passage **1** where the circulating hydrogen in the state of ordinary temperature flows. Then, the excessive circulating hydrogen is supplied to a portion in the raw hydrogen passage **11** of the liquid hydrogen producing unit P where the raw hydrogen in the state of ordinary temperature flows and is mixed with the raw hydrogen. Thus, the boil-off gas is re-liquefied and reused as liquid hydrogen.

[0033] The boil-off gas treating mechanism includes a boil-off gas supplying member C and a circulating hydrogen discharge member D. The boil-off gas supplying member C supplies the boil-off gas in the state of very low temperature generated in the liquid hydrogen vessel of the liquid hydrogen transporting ship **16**, to the hydrogen circulating passage **1** at a position downstream of the expansion turbine **4** and upstream of the compressor **2**. As described later in detail, the boil-off gas supplying member C shifts the position through which the boil-off gas is supplied to the hydrogen circulating passage **1** depending on the temperature of the boil-off gas in such a manner that the difference between the temperature of the circulating hydrogen at the position through which the boil-off gas is supplied and the temperature of the boil-off gas is minimized.

[0034] On the other hand, the circulating hydrogen discharge member D discharges the circulating hydrogen in the state of ordinary temperature in the hydrogen circulating passage **1** to the raw hydrogen passage **11** at a position upstream of the first raw hydrogen cooling element **13** with respect to the direction along which the raw hydrogen flows. Thus, the discharged circulating hydrogen is mixed with the raw hydrogen in the state of ordinary temperature. That is, the circulating hydrogen discharge member D discharges the excessive circulating hydrogen resulting from the supply of the boil-off gas to the raw hydrogen passage **11** through the portion between the first low-temperature heat exchanging element **5** and the compressor **2** in the hydrogen circulating passage **1**, or through the portion between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7** in the hydrogen circulating passage **1**. However, in the embodiment shown in FIG. **1**, the excessive circulating hydrogen is discharged to the raw hydrogen passage **11** through the portion between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7** in the hydrogen circulating passage **1**.

[0035] Hereinafter, concrete structure and function of the boil-off gas treating mechanism will be described. The boil-off gas supplying member C has a boil-off gas introducing passage **17** through which the boil-off gas in the state of ordinary pressure (for example, 0.1 MPaA) and very low temperature generated in the liquid hydrogen vessel of the liquid hydrogen transporting ship **16** is pipe-transported to the liquid hydrogen producing apparatus HS. The circumference of the boil-off gas introducing passage **17** is insulated in order to prevent the temperature of the boil-off gas from increasing due to heat inputted from the outside although such an insulator is not shown in FIG. **1**. Moreover, a first boil-off gas supplying passage **19** and a second boil-off gas supplying passage **20** are connected through a changeover valve **18** to the downstream end of the boil-off gas introducing passage **17** with respect to the direction along which the boil-off gas flows. The changeover valve **18** alternatively connects the boil-off gas introducing passage **17** to either of the first boil-off gas supplying passage **19** or the second boil-off gas supplying passage **20**, or closes the boil-off gas introducing passage **17**.

[0036] The downstream end of the first boil-off gas supplying passage **19** is connected to the hydrogen circulating passage **1** at a position between the first low-temperature heat exchanging element **5** and the second low-temperature heat exchanging element **6** with respect to the direction along which the boil-off gas flows. Meanwhile, the downstream end of the second boil-off gas supplying passage **20** is connected to the hydrogen circulating passage **1** at a position between the second low-temperature heat exchanging element **6** and the expansion turbine **4** with respect to the direction along which the boil-off gas flows. Accordingly, the boil-off gas supplying member C can alternatively supply the boil-off gas in the boil-off gas introducing passage **17** to either of the hydrogen circulating passage **1** at the position between the first low-temperature heat exchanging element **5** and the second low-temperature heat exchanging element **6** or the position between the second low-temperature heat exchanging element **6** and the expansion turbine **4** by changing the passage-connecting condition of the changeover valve **18**.

[0037] Moreover, the boil-off gas introducing passage **17** is equipped with a blower **21** (or a compressor) with a very low compression ratio for making the boil-off gas flow downstream, a first flow rate sensor **22** for detecting the flow rate of the boil-off gas flowing through the boil-off gas introducing passage **17** and a temperature sensor **23** for detecting the temperature of the boil-off gas, which are disposed in turn toward the downstream side in the positions upstream of the changeover valve **18** with respect to the direction along which the boil-off gas flows. The data values detected by the first flow rate sensor **22** and the data values detected by the temperature sensor **23** are transmitted to a controller **24** described later in detail. The boil-off gas generated in the liquid hydrogen vessel of the liquid hydrogen transporting ship **16** is in the state of ordinary pressure. Meanwhile, the circulating hydrogen in the hydrogen circulating passage **1** is also in the state of ordinary pressure at the position where the boil-off gas is supplied thereto. Accordingly, the blower **21** with very low compression ratio can easily supply the boil-off gas to the hydrogen circulating passage **1**. Because the boil-off gas is hardly compressed on that occasion, the temperature of the boil-off gas is hardly changed upward. Meanwhile, if the pressure of the boil-off gas is higher than the pressure of the circulating hydrogen at the position where the boil-gas is supplied thereto, the blower **21** may be omitted.

[0038] On the other hand, the circulating hydrogen discharge member D has a circulating hydrogen discharge passage **26** which connects a portion of the hydrogen circulating passage **1** to a portion of the raw hydrogen passage **11** through a change valve **25**, the portion of the hydrogen circulating passage **1** being located between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7**, and the portion of the raw hydrogen passage **11** being located upstream of the first raw hydrogen cooling element **13** with respect to the direction along which the raw hydrogen flows. The change valve **25** connects the portion of the hydrogen circulating passage **1** between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7** to the circulating hydrogen discharge passage **26**, or interrupts the connection between the hydrogen circulating passage **1** and the circulating hydrogen discharge passage **26**.

[0039] Moreover, the circulation hydrogen discharge passage **26** is equipped with a compressor **27** for making the discharged circulating hydrogen flow downstream, a flow control valve **28** for controlling the flow rate of the circulating hydrogen flowing through the circulation hydrogen discharge passage **26** and a second flow rate sensor **29** for detecting the flow rate of the circulating hydrogen flowing through the circulation hydrogen discharge passage **26**. These members **27**, **28** and **29** are disposed in turn toward the downstream side with respect to the direction along which the circulating hydrogen is discharged from the hydrogen circulating passage **1**. The data values detected by the second flow rate sensor **29** are transmitted to the controller **24**. Each of the circulating hydrogen in the hydrogen circulating pas sage **1** at the position between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7** and the raw hydrogen in the raw hydrogen passage **11** at the position upstream of the first raw hydrogen cooling element **13** is in the state of high pressure. However, because the pressure of the above-mentioned circulating hydrogen and the pressure of the above-mentioned raw hydrogen are almost identical to each other, the compressor **27** can easily discharge the circulating hydrogen to the raw hydrogen passage **11** even if the compression ratio of the compressor **27** is very low. Because the circulating hydrogen is hardly compressed on that occasion, the temperature of the circulating hydrogen is hardly changed upward. Meanwhile, if the pressure of the circulating hydrogen at the above-mentioned position is higher than the pressure of the raw hydrogen, the compressor **27** may be omitted.

[0040] The controller **24**, which is a comprehensive controlling device having a computer for the boil-off gas treating mechanism, controls the changeover valve **18**, the blower **21**, the change valve **25**, the compressor **27** and the flow rate control valve **28** by using the control information including the flow rate of the boil-off gas detected by the first flow rate sensor **22**, the temperature of the boil-off gas detected by the temperature sensor **23** and the flow rate of the circulating hydrogen detected by the second flow rate sensor **29**. Control procedures of the boil-off gas treating mechanism, which is executed by the controller **24**, will be concretely described hereinafter.

[0041] After the liquid hydrogen transporting ship **16**, whose liquid hydrogen vessel holds a suitable amount (for example, a few percent in volume with respect to the volume of the liquid hydrogen vessel of the ship) of liquid hydrogen for keeping the liquid hydrogen vessel cold, has reached the shipping port near the liquid hydrogen storage tank **15** and has harbored therein, the liquid hydrogen stored in the liquid hydrogen storage tank **15** is supplied to the liquid hydrogen vessel of the liquid hydrogen transporting ship **16** (referred to as "ship vessel" hereinafter). Meanwhile, in general, it is estimated that the liquid hydrogen transporting ship **16** will be harboring within a short time of one day or a few days. On that occasion, it is estimated that the temperature of the ship vessel, particularly the temperature in the upper portion of the ship vessel has become higher than the saturation temperature of the liquid hydrogen because heat outside of the ship vessel was transmitted to the ship vessel when the liquid hydrogen transporting ship **16** was traveling or harboring.

[0042] In consequence, the supplied liquid hydrogen is partially vaporized resulting from the difference between the temperature of the ship vessel and the temperature of the supplied liquid hydrogen so that boil-off gas of large amounts is generated within a short time. In general, the temperature of the boil-off gas generated in the ship vessel may be 50-80K when it has been started to supply the liquid hydrogen. Then, when the filling fraction of the liquid hydrogen in the ship vessel becomes larger, the ship vessel is cooled by the liquid hydrogen. Thus, because the temperature of the ship vessel is gradually lowered, the temperature of the boil-off gas is lowered to become 20-50K, which is a temperature near the temperature at which hydrogen may be liquefied.

[0043] Thus, the blower **21** is activated by the controller **24** so that the boil-off gas in the state of very low temperature (for example, 20-80K) generated in the ship vessel is supplied to the liquid hydrogen producing apparatus HS through the boil-off gas introducing passage while approximately maintaining its temperature. On that occasion, if the temperature of the boil-off gas detected by the temperature sensor **23** is in a relatively high range equal to or higher than 50K, for example in the range from 50K to 80K, the controller **24** controls the changeover valve **18** in such a manner that the boil-off gas introducing passage **17** is connected to the first boil-off gas supply passage **19**. On the other hand, if the temperature of the boil-off gas detected by the temperature sensor **23** is in a relatively low range lower than 50K, for example in the range from 20K to 50K (except the just point of 50K), the controller **24** controls the changeover valve **18** in such a manner that the boil-off gas introducing passage **17** is connected to the second boil-off gas supplying passage **20**. Meanwhile, when the boil-off gas is not supplied to the liquid hydrogen producing apparatus HS, the controller **24** shuts down the blower **21** and controls the changeover valve **18** in such a manner that the boil-off gas introducing passage **17** is closed.

[0044] In other words, when the temperature of the boil-off gas is relatively high, for example in the range from 50K to 80K, the boil-off gas is mixed with the circulating hydrogen, for example in the state of 80K in the hydrogen circulating passage **1** at the position between the first low-temperature heat exchanging element **5** and the second low-temperature heat exchanging element **6**. On the other hand, when the temperature of the boil-off gas is relatively low, for example in the range from 20K to 50K (except the just point of 50K), the boil-off gas is mixed with the circulating hydrogen, for example in the state of 20K in the hydrogen circulating passage **1** at the position between the second low-temperature heat exchanging element **6** and the expansion turbine **4**. Thus, the portion of the hydrogen circulating passage **1**, to which the boil-off gas is supplied, is shifted depending on the temperature of the boil-off gas in such a manner that the difference between the temperature of the circulating hydrogen at the portion to which the boil-off gas is supplied and the temperature of the boil-off gas is minimized. In consequence, the boil-off gas does not particularly affect the temperature distribution of the circulating hydrogen in the hydrogen circulating passage **1**. Because the boil-off gas is supplied to the hydrogen circulating passage **1** in the state of very low temperature, which is similar to the state that the boil-off gas has been generated in the ship vessel as described above, the cold heat of the boil-off gas is not wasted.

[0045] If the boil-off gas is supplied to the hydrogen circulating passage **1** in the state of very low temperature which is similar to the state that the boil-off gas has been generated in the ship vessel, the energy efficiency of the liquid hydrogen producing apparatus HS is highly improved in comparison with such a case that the boil-off gas is at first heated to ordinary temperature (300K) and then supplied to the raw hydrogen passage **11**. If the flow rate and temperature of the boil-off gas is, for example 0.53 kg/s and 20K, respectively, it is possible to reduce about 2.1 MW of energy as shown by the expression described below because the heat capacity of hydrogen is 14.4 kJ/(kg·K). Thus, if it is assumed that the power consumption of the liquid hydrogen producing apparatus HS is 20.0 MW, it is expected that the energy efficiency is improved by about 10.5%.

$$14.4\ [\mathrm{kJ/(kg \cdot K)}] \times 0.53\ [\mathrm{kg/s}] \times 280\ [\mathrm{K}] = 2130\ [\mathrm{kJ/s}] = 2.1\ [\mathrm{MW}]$$

[0046] If the number of the heat exchangers is larger than two, the number of the boil-off gas supplying passages may be increased depending on the number of the heat exchangers while the changeover valve may be adapted to alternatively connect the boil-off gas introducing passage **17** to each of the boil-off gas supplying passages. Thus, the controller **24** may control this changeover valve depending on the temperature of the boil-off gas in such a manner that the difference between the temperature of the circulating hydrogen at the position through which the boil-off gas is supplied and the temperature of the boil-off gas is minimized.

[0047] For example, in such a case that the number of the heat exchangers is N (N≥3), namely the number of the low-temperature heat exchanging elements is N, N-number of boil-off gas supplying passages in total are connected to the respective portions in the hydrogen circulating passage **1**, the portions being located between respective adjacent low-temperature heat exchanging elements or between the most upstream low-temperature heat exchanging element and the expansion turbine **4**. In this case, the changeover valve may alternatively select one of the N-number of boil-off gas supplying passages. However, in the case that the number of the heat exchangers is N (N≥3), the number of the boil-off gas supplying passages may be smaller than N as long as the number is not smaller than 2.

[0048] When the boil-off gas is supplied to the hydrogen circulating passage **1** as described above, the amount of the circulating hydrogen in the hydrogen circulating passage **1** is excessively increased depending on the amount of the supplied boil-off gas so that the hydrogen circulating passage **1** holds excessive circulating hydrogen. Thus, when the boil-off gas is supplied to the hydrogen circulating passage **1**, the controller **24** activates the compressor **27** while controlling the change valve **25** in such a manner that the hydrogen circulating passage **1** between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7** is connected to the circulation hydrogen discharge passage **26**.

[0049] In addition, the controller **24** controls the flow rate control valve **28** in such a manner that the flow rate of the circulating hydrogen detected by the second flow rate sensor **29** coincides with the flow rate of the boil-off gas detected by the first flow rate sensor **22**. In this case, for example, the controller **24** changes the degree of opening of the flow rate control valve **28**. In consequence, the circulating hydrogen, whose amount is as same as the amount of the boil-off gas supplied to the hydrogen circulating passage **1**, is discharged from the hydrogen circulating passage **1** to the raw hydrogen passage **11**, and then mixed with the raw hydrogen. Accordingly, the amount of the circulating hydrogen in the hydrogen circulating passage **1** is maintained at an appropriate level. If the boil-off gas is not supplied from the ship vessel to the hydrogen circulating passage **1**, the controller **24** shuts down the compressor **27** while controlling the change valve **25** in such a manner that the hydrogen circulating passage **1** is disconnected to the circulation hydrogen discharge passage **26**.

[0050] Because the circulating hydrogen discharged from the hydrogen circulating passage **1** to the raw hydrogen passage **11** through the circulation hydrogen discharge passage **26** is in the state of ordinary temperature, the discharged circulating hydrogen does not lower the temperature of the raw hydrogen flowing through the raw hydrogen passage **11**. Accordingly, when the circulating hydrogen is mixed with the raw hydrogen in the raw hydrogen passage **11**, any trouble is not caused in the liquid hydrogen producing apparatus HS or the liquid hydrogen producing unit P which is designed on the assumption that hydrogen as the raw material is supplied at ordinary temperature.

[0051] Thus, the liquid hydrogen producing apparatus HS according to the embodiment of the present invention produces such an advantage that the boil-off gas in the state of very low temperature is supplied to the liquid hydrogen producing apparatus HS without causing any trouble in any member of the liquid hydrogen producing apparatus HS so that the liquid hydrogen whose amount corresponds to the amount of the supplied boil-off gas is produced. In other words, the large amount of boil-off gas in the state of very low temperature generated in the ship vessel in a short time is re-liquefied to become liquid hydrogen for its reuse without wasting the cold energy of the boil-off gas and with effectively utilizing the cold energy.

[0052] As described above, according to the embodiment shown in FIG. **1**, the excessive circulating hydrogen resulting from the boil-off gas supplied to the hydrogen circulating passage **1** is discharged from the hydrogen circulating passage **1** between the circulating hydrogen cooler **3** and the first high-temperature heat exchanging element **7** to the raw hydrogen passage **11** upstream of the first raw hydrogen cooling element **13** with respect to the direction along which the raw hydrogen flows. Meanwhile, the circulating hydrogen in the hydrogen circulating pas sage **1** at the portion between the first low-temperature heat exchanging element **5** and the compressor **2** is in the state of ordinary temperature. Accordingly, it is possible to provide an alternative circulating hydrogen discharge passage which connects the above-mentioned portion of the hydrogen circulating passage **1** to the portion of the raw hydrogen passage **11** upstream of the first raw hydrogen cooling element **13** with respect to the direction along which the raw hydrogen flows, and to discharge the excessive circulating hydrogen to the raw hydrogen passage **11** through the alternative circulating hydrogen discharge passage.

[0053] In this case, the circulating hydrogen in the hydrogen circulating passage **1** between the first low-temperature heat exchanging element **5** and the compressor **2** is in the state of ordinary pressure while the raw hydrogen in the raw hydrogen passage **11** is in the state of high pressure. Accordingly, it is necessary to provide a compressor and a cooler in the alternative circulating hydrogen discharge passage, the compressor being adapted to compress the circulating hydrogen in the state of ordinary pressure so as to reach the state of high pressure similar to the pressure of the raw hydrogen, and the cooler being adapted to cool the circulating hydrogen whose temperature has been elevated to a high temperature (for example, 780K) due to the adiabatic compression of the circulating hydrogen by the compressor. In this case also, it is necessary to provide a change valve, a flow rate control valve and a flow rate sensor as same as the case of the liquid hydrogen producing apparatus HS shown in FIG. **1**.

INDUSTRIAL APPLICABILITY

[0054] As described above, an apparatus for producing liquid hydrogen according to the present invention is useful for an apparatus for producing liquid hydrogen using hydrogen produced from low-grade coal such as lignite or the like, as a main raw material. In particular, the apparatus according to the present invention is suitable for re-liquefying boil-off gas generated when a liquid hydrogen vessel of a liquid hydrogen transporting ship is filled with liquid hydrogen in the case that the liquid hydrogen is transported to marked areas by the liquid hydrogen transporting ship.

EXPLANATION OF REFERENCE NUMERALS

[0055] HS Liquid hydrogen producing apparatus, R Refrigeration cycle unit, P Liquid hydrogen producing unit, E**1** First heat exchanger, E**2** Second heat exchanger, C Boil-off gas supplying member, D Circulating hydrogen discharge member, **1** Hydrogen circulating passage, **2** Compressor, **3** Circulating hydrogen cooler, **4** Expansion turbine, **5** First low-temperature heat exchanging element, **6** Second low-temperature heat exchanging element, **7** First high-temperature heat exchanging element, **8** Second high-temperature heat exchanging element, **10** Raw hydrogen supply source, **11** Raw hydrogen passage, Joule-Thomson valve, **13** First raw hydrogen cooling element, **14** Second raw hydrogen cooling element, **15** Liquid hydrogen storage tank, **16** Liquid hydrogen transporting ship, **17** Boil-off gas introducing passage, **18** Changeover valve, **19** First boil-off gas supplying passage, **20** Second boil-off gas supplying passage, **21** Blower, **22** First flow rate sensor, **23** Temperature sensor, **24** Controller, **25** Change valve, **26** Circulating hydrogen discharge passage, **27** Compressor, **28** Flow rate control valve, **29** Second flow rate sensor.

1. An apparatus for producing liquid hydrogen comprising:

a refrigeration cycle unit in which circulating hydrogen flows as a refrigerant;

a liquid hydrogen producing unit for producing the liquid hydrogen from gaseous hydrogen;

a boil-off gas supplying unit for supplying boil-off gas generated in a liquid hydrogen reservoir to said refrigeration cycle unit through a predetermined inlet portion in said refrigeration cycle unit; and

a circulating hydrogen discharge unit for discharging excessive circulating hydrogen resulting from the boil-off gas supplied to said refrigeration cycle unit by means of said boil-off gas supplying unit, to said liquid hydrogen producing unit through a predetermined outlet portion in said refrigeration cycle unit.

2. The apparatus according to claim **1**, wherein said refrigeration cycle unit comprises:

a compressor for compressing the circulating hydrogen;

an expander for expanding the circulating hydrogen; and

at least one heat exchanger interposed between said compressor and said expander, said heat exchanger including a low-temperature heat exchanging element located at an upstream side of said compressor and a high-temperature heat exchanging element located at a downstream side of said compressor,

wherein said liquid hydrogen producing unit comprises:

a raw hydrogen passage, through which the gaseous hydrogen supplied from a raw hydrogen source, flows;

an expansion valve for expanding the gaseous hydrogen to produce the liquid hydrogen, the expansion valve being disposed at a downstream side of said raw hydrogen passage; and

at least one gaseous hydrogen cooler for cooling the gaseous hydrogen by heat exchange with said at least one heat exchanger of said refrigeration cycle unit,

wherein said inlet portion in said refrigeration cycle unit is disposed at a position located downstream of said expander and upstream of said compressor, and

wherein said outlet portion in said refrigeration cycle unit is disposed at a position located between the first low-temperature heat exchanging element in an upstream direction from said compressor and the first high-temperature heat exchanging element in a downstream direction from said compressor.

3. The apparatus according to claim **1**, wherein said inlet portion in said refrigeration cycle unit is composed of a plurality of inlet elements disposed depending on differences between the temperature of the circulating hydrogen in said refrigeration cycle unit and the temperature of the boil-off gas generated in said liquid hydrogen reservoir.

4. The apparatus according to claim **1**, wherein said outlet portion in said refrigeration cycle unit is disposed between said compressor and the first high-temperature heat exchanging element in a downstream direction from said compressor.

5. The apparatus according to claim **1**, wherein said expander is an expansion turbine.

6. The apparatus according to claim **1**, wherein said expansion valve is a Joule-Thomson valve.

7. The apparatus according to claim **1**, wherein said liquid hydrogen reservoir is a liquid hydrogen vessel of a liquid hydrogen transporting ship.

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