Technologies of hydrogen liquefaction, transport and storage – Paving the way to a hydrogen fueled future

Demand for hydrogen is expected to increase as we head toward becoming a hydrogen economy. With a view to realizing the Hydrogen Energy Supply Chain Initiative, which envisions importing hydrogen produced in Australia, Kawasaki is developing related equipment. Before commercial operation of the hydrogen energy chain, Kawasaki is planning to implement a small-scale pilot chain around 2020, and a large-scale demonstration chain between 2025 and 2030. When importing hydrogen gas, it will be converted into LH_2 (liquefied hydrogen) suitable for large-scale transport and storage. The technology used for liquefaction, transport, and storage is derived from the cryogenic technology Kawasaki has built up through the development of rocket launch complexes and LNG carries.

Technological development to realize the chain concept is steadily progressing. In terms of liquefaction technology, Kawasaki has succeeded in hydrogen liquefaction using Japan's first large-scale hydrogen liquefier. In terms of transport technology, Kawasaki has obtained approval in principle for the cargo containment system to be installed on the world's first LH_2 carrier.

Preface

Commercialization of hydrogen usage systems and development of infrastructure-related technology are stepping up in Japan and overseas, in a move to build a hydrogen society that will resolve the environmental issues of global warming and resource depletion. Kawasaki proposed the concept of a hydrogen energy supply chain in 2010 and has been working toward its realization. This report discusses the background to the Kawasaki supply chain concept, the predicted expansion of future hydrogen demand, and the state of Kawasaki's achievements and technical developments relating to the liquefaction of hydrogen and the transportation and storage of LH_2 that comprise the supply chain.

1 Background

The Strategic Energy Plan[1)] approved by the Japanese Cabinet in April 2014 stipulated initiatives to realize a hydrogen society. With regards to hydrogen business, fuel cell vehicles (FCV) went on sale at the end of 2014, one year ahead of schedule. Furthermore, in the lead up to COP21 at the end of 2015, the EU announced in February 2015 the long-term target of reducing global greenhouse gas emissions by at least 60% in comparison to 2010 levels by 2050. Amidst such conditions, expectations in the hydrogen society are steadily mounting.

The French science fiction author Jules Verne first predicted a hydrogen society in his 1874 novel, The Mysterious Island. A century later in 1974, the first World Hydrogen Energy Conference (WHEC) was held, and scientific discussion of the subject began in earnest. Since then, hydrogen energy systems have been proposed around the world as a means to complement electric power systems.

In Kawasaki's concept of a hydrogen energy supply chain, hydrogen is manufactured from lignite in Australia, the CO_2 generated is captured and stored on-site, and CO_2-free hydrogen is imported into Japan. Kawasaki has proposed this concept and is working toward its realization in preparation for increased hydrogen demand in the coming hydrogen society.

2 Future hydrogen demand increases

In the hydrogen society, demand for hydrogen will rapidly increase as applications for hydrogen expand from the stationary fuel cells and FCV already at the stage of commercialization, to hydrogen engines and gas turbines for power generation. Japanese research institutions, have predicted hydrogen demand according to various CO_2 restrictions and energy technology evaluation models. For example, The Institute of Applied Energy assumes a CO_2 emissions reduction of 5% of 1990 levels by 2020, and 80% by 2050, and goes on to predict hydrogen demands hypothesizing hydrogen derived from overseas lignite, natural gas, and wind power. The predicted demand reaches 2.5 Mtoe (megaton of oil equivalent) (approximately 9.7 billion Nm^3/y of hydrogen) in 2030 and 57 Mtoe (approximately 219.8 billion Nm^3/y of hydrogen) in 2050.

3 Hydrogen imports from overseas

The idea of importing hydrogen from overseas has been investigated in Japan and other countries for over 20 years[2)]. Table 1 shows the transportation route, hydrogen source and form of hydrogen transported for each project. As shown by the table, the form of hydrogen transported is LH_2 in most cases. Two representative projects are the Euro-Quebec Hydro-Hydrogen Pilot Project (EQHHPP, 1986-1998) and Japan's International Clean Energy Network Using Hydrogen Conversion (World Energy Network (WE-NET), 1993-2003), both of which used renewable energy as a hydrogen source. The EQHHPP split water at a 100 MW hydro plant in Quebec, Canada, and transported the LH_2 produced to Hamburg, Germany by sea. The amount of hydrogen transported was 1.5×10^4 t/y (167 million Nm^3/y). The WE-NET adopted LH_2 as the medium for hydrogen transportation in the same way as the EQHHPP, but at a scale of about 10 times larger.

4 The Kawasaki hydrogen energy supply chain concept

In 2010, Kawasaki announced its concept of a CO_2-free hydrogen energy supply chain, by which cheap hydrogen is produced from lignite in Victoria, Australia, and transported for use in Japan. The concept was also specified as a future hydrogen energy chain in the Japanese Ministry of Economy, Trade and Industry's Strategic Road Map for

Table 1 Overseas hydrogen import projects

Project	Transportation route	Hydrogen source	Form of hydrogen transported
EQHHPP	Canada - Europe	Hydro	LH_2, MCH, NH_3
NHGE	Norway - Europe	Hydro	LH_2
EURO-HYPORT	Iceland - Europe	Hydro/geothermal	LH_2
HYSOLAR	Germany - Saudi Arabia	Solar	LH_2
HIHEPP	Hawaii - other countries	Tidal	–
Wind power	Argentina - other countries	Wind	LH_2
Glacier	Greenland	Hydro, glacier	LH_2
WE-NET	Canada - Japan	Hydro	LH_2, NH_3, CH_3OH

Notes: LH_2: liquefied hydrogen, MCH: methylcyclohexane, NH_3: ammonia, CH_3OH: methanol

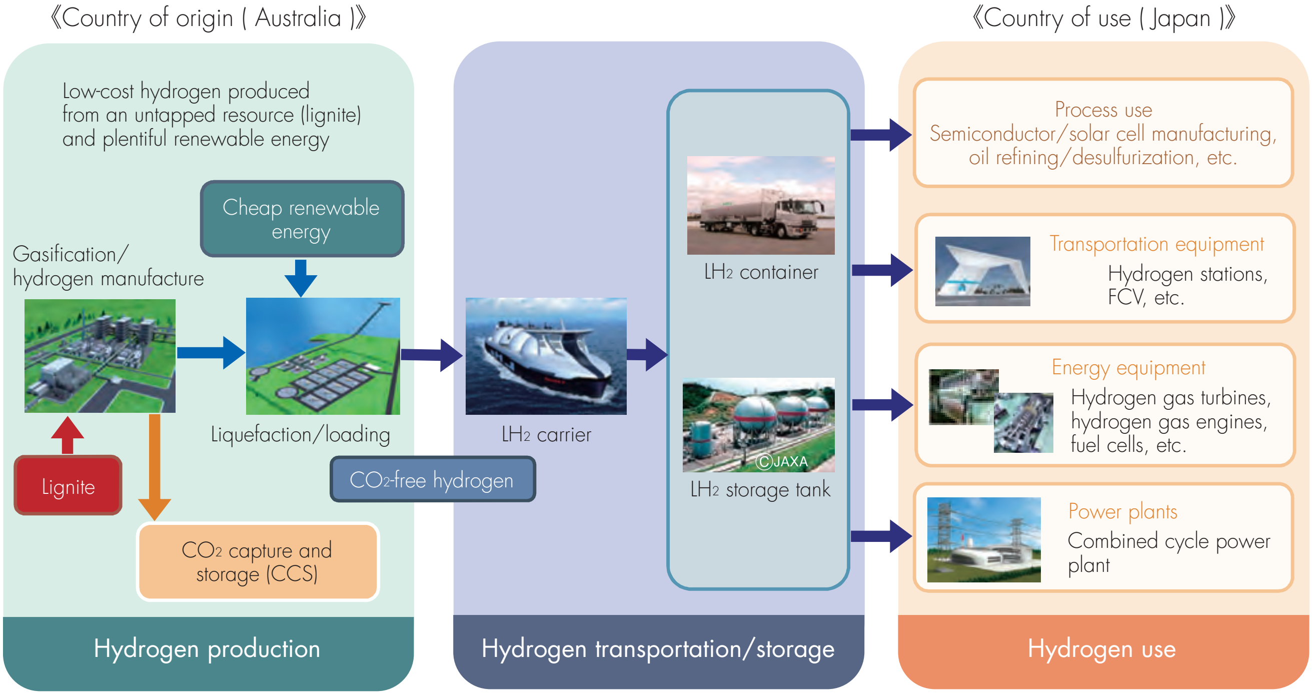

Fig. 1 The concept of a hydrogen energy supply chain

Hydrogen and Fuel Cells published in June 2014. Figure 1 gives a conceptual diagram of the system. Hydrogen is produced from Australian lignite by gasification and purification, after which it is liquefied and transported by ship to Japan. Cheap, CO_2-free hydrogen with no associated CO_2 emissions is imported, because the CO_2 gas produced in the gasification process undergoes CO_2 capture and storage (CCS) in Australia. The imported LH_2 is used as a fuel in a hydrogen power plant adjacent to the receiving terminal and is distributed to hydrogen stations for FCV and to energy equipment such as hydrogen engines in various locations.

Lignite is an underexploited form of coal limited to use in power plants close to the excavation site due to having a high water content (approximately 60%) in comparison to bituminous coal and therefore a low transportation efficiency, and also because it tends to become spontaneously combustible when dry. A vast quantity exists in Victoria, Australia, making hydrogen production possible at an extremely low cost.

5 Hydrogen infrastructure

Kawasaki is promoting the development of a hydrogen infrastructure in a move towards the realization of a hydrogen society. This specifically comprises hydrogen liquefaction systems to convert gaseous hydrogen into a liquid, tanks to store the LH_2, containers and ships to transport the LH_2, and the like.

This infrastructure is highly compatible with Kawasaki's current business, because it can be realized by building on the LNG technology, cryogenic technology, and large-scale construction technology Kawasaki has cultivated to date, such as LNG carriers and the LH_2 tanks of the Japan Aerospace Exploration Agency (JAXA) Tanegashima Space Center.

Of these, we will describe in detail the hydrogen liquefaction system, the first for industrial use comprising entirely Japanese proprietary technologies.

6 Hydrogen liquefaction system

The hydrogen gas produced from lignite is refined to a high purity and pressure-fed to a hydrogen liquefaction system by pipeline. The hydrogen gas is cooled to approximately 20 K (-253°C) and liquefied by a hydrogen liquefier. The LH_2 is loaded into containers and tank trucks equipped with thermal insulated tanks, and transported to the shipping terminal. In a large-scale chain, the hydrogen gas is sent to the shipping terminal by pipeline, and liquefied by a hydrogen liquefier established at the terminal. At the shipping terminal, the LH_2 is temporarily stored in a tank, before being loaded onto a carrier by liquid pump and transported to Japan by sea. After arrival in Japan, it is stored in an LH_2 tank at the receiving terminal and distributed from the tank to hydrogen usage systems at various locations. The scale of the hydrogen liquefaction system from liquefaction to storage and transportation is determined according to hydrogen demand and output volumes and the number of days required for marine transportation. The properties of LH_2 and a description of the hydrogen gas liquefaction and the storage and transportation apparatus for LH_2 in the hydrogen liquefaction system are given below.

(1) Properties of LH_2

Media by which hydrogen can be transported and stored include LH_2, compressed hydrogen gas, hydrogen storage alloys, and chemical media, but only compressed hydrogen gas and LH_2 are developed to the level of commercial application. Hydrogen storage alloys and chemical media require an external source of energy in the dehydrogenation process to retrieve the hydrogen, but LH_2 only requires energy input during liquefaction and does not require any extra energy for gasification in the hydrogen usage system.

Technological development of LH_2 began from bubble chamber experiments in the field of high-energy physics in the 1950s and rapidly developed alongside NASA's rocket fuel technologies. A 30 t/d hydrogen liquefier was constructed in the late 1950s, and a 60 t/d hydrogen liquefier, the largest in the world at the time, and an LH_2 storage tank with a capacity of 3,200 m^3 were constructed in the 1960s. In Japan, LH_2 began to be used primarily as a rocket fuel from the 1980s. Currently, its use is expanding in semiconductor and other industrial fields.

In the hydrogen society, LH_2 will be brought in on a large scale, so technology for liquefied natural gas will be used (LNG; main component: methane), which is similarly a flammable liquefied gas and has been at a commercial level since the 1960s. Table 2 shows a comparison of the properties of LH_2 and LNG. The saturated liquid density of LH_2 (70.8 kg/m^3) is approximately 790 times its gas density at atmospheric pressure and 0°C (0.0899 kg/Nm^3), and approximately 1.7 times its compressed gas density at 70MPa and 0°C (42.1 kg/m^3). Therefore, the volumetric efficiency of LH_2 is extremely high. Also, the boiling point of LH_2 (20.3 K) is around 90°C lower than that of LNG (112 K), and its latent heat per unit volume is small. Thermal insulation technology more advanced than that for LNG and liquefaction technology that reduces power requirements are necessary.

A significant feature of hydrogen is that it exists as high-energy-level ortho-hydrogen and low-energy-level para-hydrogen, according to the spin direction of the nucleus. Hydrogen gas at room temperature is normal hydrogen comprising 25% para-hydrogen and 75% ortho-hydrogen, whereas LH_2 is 99.8% para-hydrogen. In the liquefaction process from normal hydrogen to LH_2, it is important to maintain the equilibrium-state ortho-para composition ratio during the pre-cooling process. Also, the critical pressure for LH_2 (1.28 MPa) is smaller than that of LNG (4.6 MPa), and it is important to take into account significant physical changes near the critical condition.

Table 2 Comparison of LH_2 and LNG

		LH_2	LNG(CH_4)
Boiling point (K)		20.3 (-253°C)	112(-162°C)
Gas density (kg/Nm^3)		0.0899	0.717
Saturated liquid density (kg/m^3)		70.8	442.5
Saturated gas density (kg/m^3)		1.34	1.82
Critical temperature (K)		32.9	190
Critical pressure (MPa)		1.28	4.6
Latent heat	Per unit volume (kJ/L)	31.4	226
	Per unit weight (kJ/kg)	444	510
Lower heating value	Per unit volume (MJ/L)	8.5	22.1
	Per unit weight (MJ/kg)	120	50

Notes: • Physical properties of methane used for natural gas
• Physical properties at atmospheric pressure used for saturated liquid and saturated gas

(2) Liquefaction of hydrogen gas

The minimum liquefaction work required to turn hydrogen gas into a liquid (exergy) is thermodynamically determined by the state quantity at the start and the end of the liquefaction process. Assuming a start point of atmospheric pressure and 300 K and an end point of saturated LH_2 at atmospheric pressure, the minimum liquefaction work is approximately 3.90 kWh/kg (0.35 kWh/Nm^3), around 10 times that of LNG (methane).

The breakdown of the minimum liquefaction work for hydrogen gas is as follows.

① The work to pre-cool the hydrogen gas at normal temperature (300 K) to saturated hydrogen gas (20 K)

② The work to condense the saturated gas into a saturated liquid

③ The work for ortho/para conversion to convert room temperature hydrogen into LH_2 (99.8% para-hydrogen)

The work comprised by pre-cooling is 41%, condensation is 44%, and ortho/para conversion is 15%[3]. In comparison to LNG liquefaction work, the proportion of pre-cooling work is large and ortho-para conversion forms extra work.

Figure 2 shows an example liquefaction system composition (Claude cycle) for a liquefier. The process comprises a refrigeration cycle to produce cold energy and a hydrogen gas supply system that uses the cold energy to cool and liquefy normal temperature hydrogen gas. The cold energy for the cooling cycle is generated by refrigerant (hydrogen, helium, etc.) compressed to a high pressure by a compressor expanding in an expansion turbine (isentropic expansion).

In the hydrogen gas supply system, manufactured hydrogen gas refined to a high purity is compressed by a compressor and gradually cooled by a heat exchanger from normal temperature to around the temperature of LH_2 using the cold energy of the refrigeration cycle. The cooled compressed gas expands to around atmospheric pressure (isenthalpic expansion) and liquefies by means of an expansion valve. The heat exchanger, expansion valve, expansion turbine, and other components are kept in a cold box (vacuum chamber) to isolate them from heat input.

Actual liquefaction work is in the order of approximately 1 kWh/Nm^3, and liquefaction efficiency (minimum liquefaction work/actual liquefaction work) is around the order of 30%. This case is based on the raw material hydrogen being at atmospheric pressure and 300 K, but if a high-pressure raw material hydrogen gas is supplied, both the minimum liquefaction work and the actual liquefaction

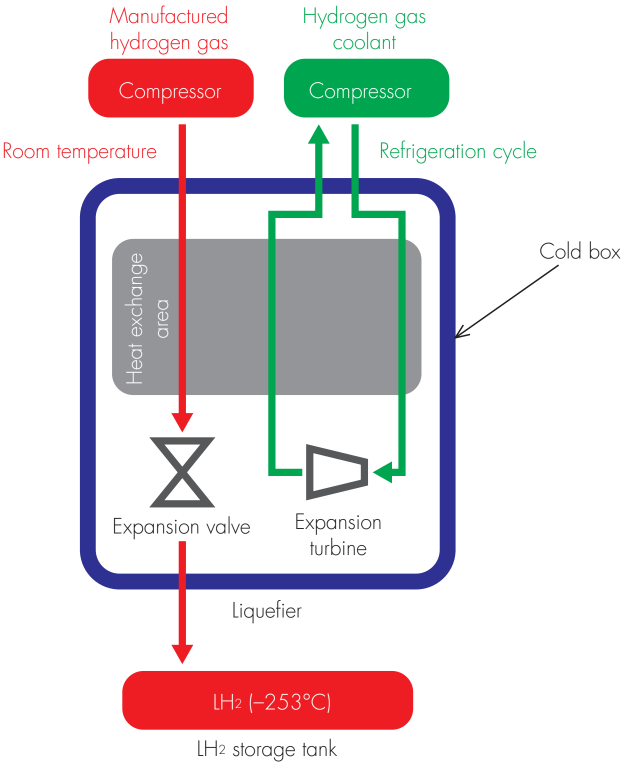

Fig. 2 Composition of hydrogen liquefaction system

Fig.3 Japan's first-large scale hydrogen liquefier

work decrease.

Figure 3 shows the appearance of Japan's first large-scale 5 t/d-class hydrogen liquefier developed by Kawasaki. A gas-bearing expansion turbine was adopted for the expander, and helium liquefier technology (boiling point 4.3 K) developed by Kawasaki in the 1980s was used in the liquefier. The adoption of a gas-bearing expansion turbine enabled high-efficiency liquefaction because high-speed revolution and a high expansion rate are achieved, in addition to it having no system contamination or complexity in restarting, which are issues in oil-bearing expansion turbines. Currently, we are evaluating and testing the components while running test operations.

(3) Storage of LH_2

Thermal insulation technology is particularly important to reduce evaporation in the storage and transportation of LH_2, which has a low boiling point and a low latent heat. A normal pressure solid insulation construction (urethane foam, etc) is adopted for the insulation of LNG tanks, but high-vacuum insulation (under 10^{-2} Pa) is often used with small and medium-size LH_2 tanks (capacity 20-300 m^3) and low-vacuum insulation (under 1 Pa) is often used with larger tanks to drastically reduce the heat input. The input heat flux is approximately 1 W/m^2, but for a larger tank with the same input heat flux, the ratio of surface area to volume decreases and the fluid evaporation rate (%/d) is mitigated. Figure 4 shows the appearance of the largest LH_2 tank in Japan (capacity 600 m^3), which Kawasaki constructed for the Japanese Aerospace Exploration Agency's (JAXA) Tanegashima Space Center. This LH_2 tank has a double-shell construction employing perlite for low-vacuum insulation and an evaporation rate of not more than 0.18%/d. NASA's 3,200 m^3 LH_2 tank, the largest in the world, is also a double-shell tank employing the same insulation method.

The capacity of the aboveground LH_2 tanks for a pilot CO_2-free hydrogen chain and a demonstration chain is planned to be approximately 3,400 m^3 and 50,000 m^3, respectively, and the technologies of the LH_2 tanks


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Fig.4 Japan's largest LH_2 tank

Fig.5 Trial manufacture of aboveground LH_2 tank

Kawasaki has constructed will be incorporated.

Kawasaki is currently prototyping an aboveground LH_2 tank at its Harima Works as shown in Fig. 5. This tank brings together the cryogenic technologies and manufacturing capabilities the company has accumulated to date, and Kawasaki is aiming to make it commercially viable at an early stage.

(4) LH_2 transportation

The transportation of LH_2 is categorized as land transportation and sea transportation. Land transportation is generally by trucks with an integrated tank or a separable container. In contrast to stationary tanks, the LH_2 tanks for transportation must have a thin layer of insulation between the inner and outer tanks in order to increase volumetric efficiency to a maximum, and must have a special supporting structure to withstand the weight of the load and reduce heat input.

(i) Land transportation

Figure 6 shows a 40-ft container developed by Kawasaki. The container is made up of a container frame (W2.4 m x H2.6 m x L12 m) housing a tank comprising an inner tank (capacity 46 m^3) and an outer tank. High vacuum insulation using multilayer insulation material is employed. The evaporation rate is 1.0%/d or less. This container is used to transport LH_2 across land from a liquefaction terminal in Japan to semiconductor factories, the JAXA Tanegashima Space Center, and other locations.

Fig.6 LH_2 container

(ii) Sea transportation

There are few instances of transportation of LH_2 by sea. The EU used a large container to transport LH_2 by sea from Louisiana in the US to a rocket launch site in French Guiana, South America. Also, NASA transports LH_2 from Louisiana to a rocket engine test site by barge (capacity approximately 1,000 m^3)[3]. There are no records of the construction of an LH_2 carrier that can transport LH_2 in large volumes and over the long distance from Australia to Japan, which will be necessary in the future.

Kawasaki is developing a small LH_2 carrier for the pilot chain and a large LH_2 carrier (capacity 160,000 m^3) for the demonstration chain in a move towards the establishment of the hydrogen energy supply chain.

Concluding remarks

Government and civilian initiatives for the realization of a hydrogen society are accelerating, with moves such as infrastructure developments and the review of regulations for FCV hydrogen stations, and the establishment of a Council for a Strategy for Hydrogen and Fuel Cells with the aim of formulating a short- to medium-term hydrogen roadmap. The liquefaction of hydrogen and LH_2 transportation and storage technologies that form the foundation of Kawasaki's hydrogen energy supply chain concept for the handling of future large-volume imports of hydrogen will contribute significantly to the realization of the coming hydrogen society. Kawasaki will apply the LNG and LH_2 technologies we have accumulated over many years to promote the technological development of related equipment in a step toward the realization of economical and safe hydrogen liquefaction, transportation and storage systems.

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