Hydrogen Production
– Development of Hydrogen Production Technologies

To realize a hydrogen energy supply chain, hydrogen production technologies, which are needed at the initial stage of the supply chain, should be established. There are several methods for producing hydrogen, but as a method for producing a large amount of inexpensive hydrogen, we have focused on hydrogen production from brown-coal, which is an unutilized resource, and renewable energy. We are now working on developing and establishing the technologies necessary for these hydrogen production methods.

Introduction

The main issue in the hydrogen production phase, the initial stage of a hydrogen energy supply chain, is how inexpensively we can produce a large amount of hydrogen, but they must be CO_2-free hydrogen production technologies.

1 Background

The current major methods of hydrogen production in industry are by-product hydrogen from petrochemical plants and steelworks, and natural gas reforming. There are some facilities producing hydrogen through biomass gas reforming, but not on a big scale.

By-product hydrogen may require additional facilities to increase its purity because some impurities can get mixed in depending on the production process. Above all, the amount of production depends on the amount produced of the original product and thus by-product hydrogen is not suitable for stable mass production. Since natural gas reforming is affected by the amount produced and cost of natural gas, which is a primary source, from the viewpoint of energy security as diversification of the energy source, it would be better to produce hydrogen from other raw materials and energy resources.

Brown-coal is not being effectively used as an energy resource even though there is so much reserves of it all over the world, especially Australia. That is why Kawasaki focused on the use of brown-coal as a method of hydrogen production and has worked on establishing technologies that use it to produce a large amount of inexpensive hydrogen. With the increasing utilization of renewable energy in recent years such as wind power and photovoltaics, the price of CO_2-free electricity will become lower in the future. For this reason, we have also worked on establishing technologies that produce hydrogen by water electrolysis using such electricity.

2 Development overview

Brown-coal is an early stage coal with high water content, which makes worse transport efficiency, and it can easily cause self-ignition when it dries. It has thus only been used for power generation near mining sites, but Kawasaki is focusing on potential in brown-coal and has worked on developing hydrogen production technologies to utilize it further. As shown in **Fig. 1**, one method is to burn brown-coal in a gasifier and then only extract the hydrogen gas from the generated gases. We have tried to develop the gasification technology and the gas refining technology to extract high purity hydrogen gas, and to verify the technologies at a bench scale test facility built in one of our factories.

In hydrogen production by renewable energy, as shown in **Fig. 2**, hydrogen gas is produced by water electrolysis using electricity generated from wind power and photovoltaics. We have developed unique technologies to enable high efficiency hydrogen production, and along with this, we have conducted demonstration tests to verify the technologies attaching a small-scale prototype electrolyzer to a wind generation facility in Hokkaido.

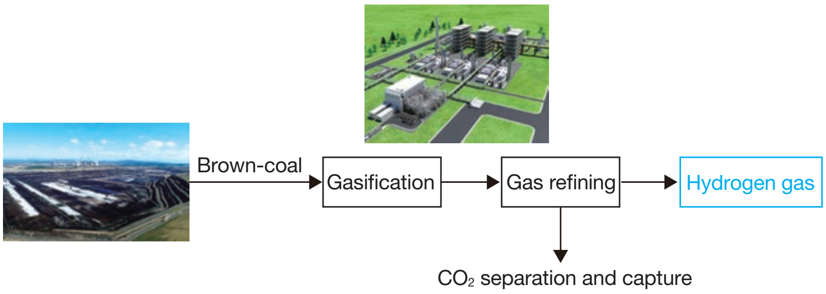

Fig. 1 Process of producing hydrogen from brown-coal

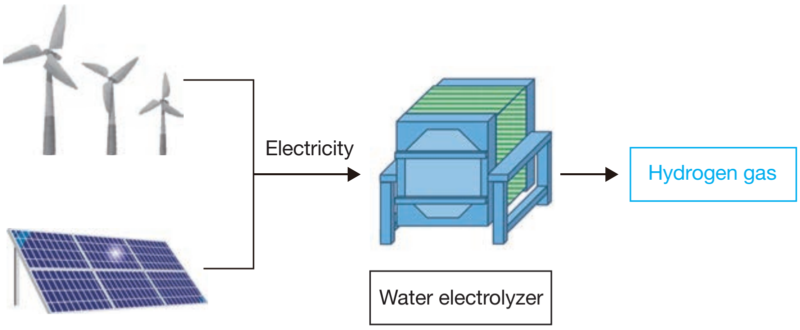

Fig. 2 Process of producing hydrogen by water electrolysis

3 Hydrogen production technology from brown-coal

(1) Hydrogen production by brown-coal gasification

The process of producing hydrogen from brown-coal consists of two major processes, as shown in **Fig. 3**. The first process is gasification to generate syngas consisting primarily of hydrogen, carbon monoxide, and carbon dioxide from raw brown-coal. The second is gas refining to remove carbon dioxide and a small amount of impurities from the syngas and then collect the hydrogen.

(i) Gasification process

In the gasification process, brown-coal pretreatment and gasification are conducted.

① Brown-coal pretreatment

We adopted a wet feed method to supply brown-coal to a pressurized gasifier. In this method, the brown-coal is broken into pieces, mixed with a dispersant and water to convert it into a liquid state called slurry as shown in **Fig. 4**, and the slurry is pumped into the gasifier.

② Gasification

In the gasification process, the brown-coal slurry is pyrolyzed by reaction heat of partial oxidation, which converts it into syngas consisting primarily of hydrogen, carbon monoxide, and carbon dioxide.

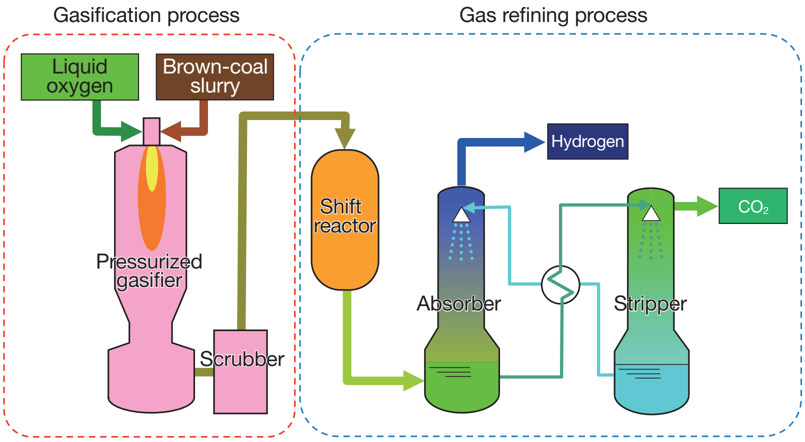

Fig. 3 Process of producing hydrogen by brown-coal gasification

(a) Raw brown-coal

(b) Brown-coal slurry

Fig. 4 Raw brown-coal and brown-coal slurry

(ii) Gas refining process

In the gas refining process, the shift reaction and CO_2 separation and capture are conducted.

① Shift reaction

In the shift reaction process, carbon monoxide, which makes up approximately 10 to 20% of the syngas, is reacted with water vapor via a catalyst to produce hydrogen and carbon dioxide, which improves the yield of hydrogen. There are two kinds of shift reaction: the sour shift reaction that requires sulfur, and the sweet shift reaction that does not.

② CO_2 separation and capture

The method of CO_2 separation and capture is selected according to the type, pressure, amount, and purity of the target gas which could be combustion emission gas or gasification gas, for example. Major methods include chemical absorption, in which CO_2 reacts with a liquid absorbent; physical absorption, in which CO_2 is dissolved in a liquid absorbent under high pressure and low temperature; adsorption, in which CO_2 is adsorbed by activated carbon or zeolite; and membrane separation in which CO_2 is separated out with a polymer membrane.

(2) Technology development

(i) Gasification process

① Brown-coal pretreatment

Although brown-coal has high water content at around 60%, we set a target of having at least 53% brown-coal in the slurry (i.e., 47% or less water content) from the standpoint of economic feasibility. In order to decrease the water content in the powdery brown-coal when mined and make the brown-coal into a highly concentrated, less viscous liquid, the surface structure had to be changed to prevent dried brown-coal from reabsorbing moisture, which is known as reforming treatment. In this project, we developed brown-coal pretreatment technologies that can dry and perform the reforming treatment on the brown-coal at the same time, which gave us a reason to adopt the wet feed method.

② Gasification

We developed a gasifier ourselves to understand the brown-coal gasification characteristic and optimize the downstream gas refining process. This gasifier has its slurry burner installed at the top where it gasifies brown-coal slurry, its wall has a fireproof heat-insulation structure, and at the bottom it has a function to directly cool the syngas. The gasifier can conduct oxygen-blown gasification in a 0.4 MPa pressurized environment, and each part is sealed with gas (CO_2) to raise the hydrogen content.

(ii) Gas Refining Process

① Shift Reaction

As brown-coal contains sulfur, the syngas generated by gasification contains sulfuric gases such as hydrogen sulfide as impurities. We thus adopted the sour shift reaction method, which does not require the removal of the sulfur content, can utilize sulfur as a catalytic activator, and is an easier system to operate.

② CO_2 separation and capture

For commercial use, the physical absorption method, which uses the pressure of a gasifier's highly pressurized gas, has a stronger track record, but because the syngas pressure supplied from the gasifier was not high enough at 0.3 MPa in our bench scale test, we adopted the chemical absorption method. Also, as a new technology, we developed a new adsorption method that uses an adsorbent with a liquid chemical absorbent supported on carrier. This method enables us to separate and capture CO_2 at a lower temperature than with the normal chemical absorption method.

(3) Technology verification through a bench scale test

As shown in **Fig. 5**, we attached a gas refining facility to a pressurized gasifier in our Akashi Works, and conducted a demonstration test for bench-scale hydrogen production from September 2012 to February 2013.

Fig. 5 Overall view of bench scale test facility

(i) Test objectives

Shift reaction equipment and CO_2 separation and capture equipment need to be combined in multiple stages to make a complete process that can be successfully established for business purposes. In our bench scale test, we tested hydrogen production from brown-coal by verifying each piece of equipment to meet capacity requirements in a single step.

(ii) Test results

Figure 6 shows the results of the test where we refined syngas generated from brown-coal in the pressurized gasifier with the shift reaction method and chemical absorption method. The amount of gas at the shift reactor outlet increased because water vapor was added, and the amount of gas at the absorber outlet decreased because CO_2 was removed. The test results were that approximately 83% of the carbon monoxide was converted in the shift reactor; almost 100% of the carbon dioxide was captured in the absorber; and a hydrogen concentration of approximately 86% was achieved. Each item met the designed value.

In addition, when we refined the gas with the shift reaction and adsorption methods we developed as new technologies, the hydrogen concentration at the adsorption outlet was over 80% and both methods met the designed value. In this way, we have successfully verified that hydrogen can be produced from brown-coal.

4 Hydrogen production technology by water electrolysis

(1) Hydrogen production by alkaline water electrolysis

Hydrogen production methods by water electrolysis can be classified into three major types: alkaline water

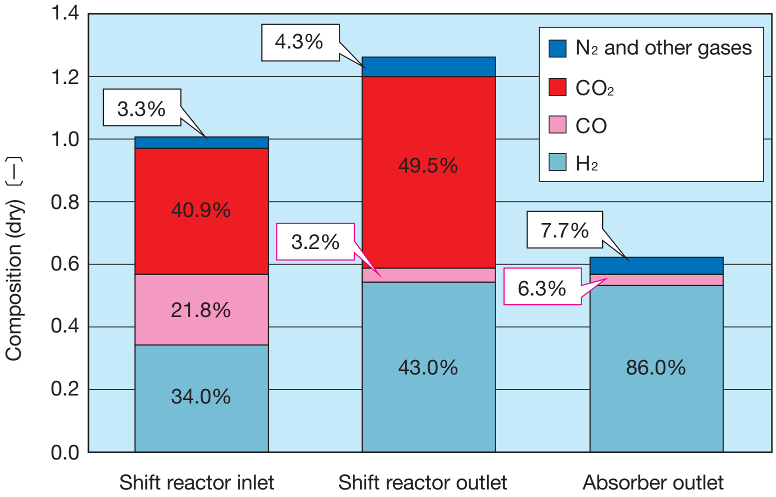

Fig. 6 Results of bench scale test — chemical absorption method

electrolysis, proton exchange membrane electrolysis, and solid oxide electrolysis [1]. The first two have reached the stage of practical use. We chose to focus our development on the alkaline water electrolysis method, which has more advantages in terms of future scalability and cost effectiveness.

Alkaline water electrolysis uses the electrolysis cell shown in **Fig. 7**, which consists of an electrolyte of potassium hydroxide solution, electrodes (an anode and a cathode), and a diaphragm. When electricity passes between the electrodes, hydrogen gas is generated at the cathode, and oxygen gas is generated at the anode.

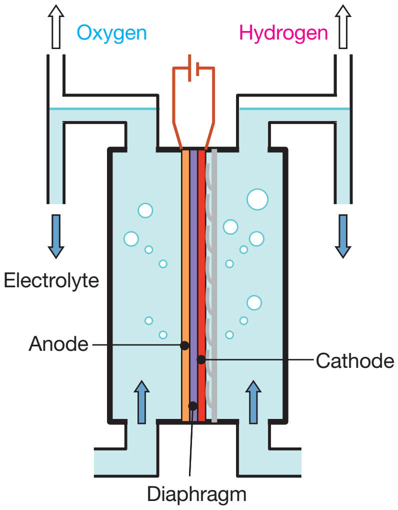

Fig. 7 Schematic diagram of alkaline water electrolysis cell

(2) Technology development

Some of the technical challenges facing alkaline water electrolysis are ensuring a high level of safety and improving electrolysis efficiency. In particular, there is a phenomenon called crossover in which a small amount of oxygen gas gets in the hydrogen gas lines. The major challenge to improving safety and ensuring that high purity hydrogen gas is produced is reducing crossover as much as possible.

As electrodes greatly contribute to electrolysis efficiency, the key is to improve the catalytic activity reaction of the anodes, which generate oxygen. To increase the activation of an anode while maintaining its durability, Kawasaki has collaborated with an electrode manufacturer and a university laboratory to conduct research on topics such as optimization of a catalyzer's constituent elements and layer structure in hopes of achieving high durability and high performance.

In addition, we have researched and developed a diaphragm within our organization. While a diaphragm's gas separation ability contributes to suppressing crossover by hydrogen gas, at the same time, ion permeability is also required to improve electrolysis efficiency, and these two are in a mutually conflicting relationship. So, we optimized its constituent materials, thickness, and layer structure, and successfully developed a high-performance diaphragm that can ensure excellent performances both in ion permeability and in gas separation.

(3) Demonstration project in Hokkaido

Kawasaki conducted a demonstration operation of an alkaline water electrolyzer installed with the technologies mentioned above under a project known as, "Research and

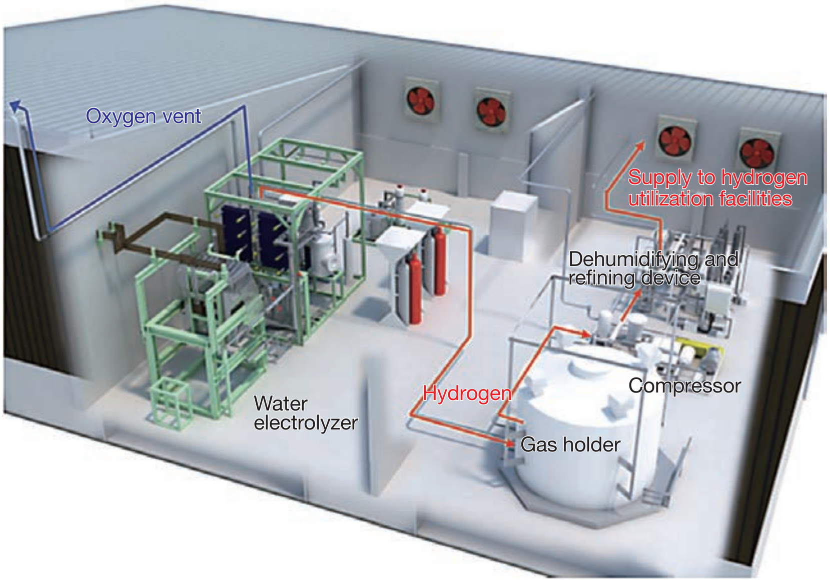

Fig. 8 Schematic image of demonstration plant (only within the scope of Kawasaki Heavy Industries, Ltd.)

Development on Stabilization, Storage and Utilization of Unstable Renewable Electricity In Hokkaido Using Hydrogen-Based Technologies," commissioned by the New Energy and Industrial Technology Development Organization (NEDO)[2]. In this project we attached a water electrolyzer to wind power generation facilities (a renewable energy), produced hydrogen by using part of the electricity generated there, and then demonstrated a system supplying the optimum quantity of electricity and hydrogen on demand.

Our main scope was hydrogen production using the alkaline water electrolyzer, in this system hydrogen gas produced by the electrolyzer was pressurized to 0.9 MPaG with a compressor, refined the compressed gas with a dehumidifying and refining device, and then supplied the gas to hydrogen utilization facilities (scope of one of co-implementers), as shown in **Fig. 8.**

The result of our demonstration, under the severe operating condition, which was a current density of 6.4 kA/m^2, was that electricity was provided into the alkaline water electrolyzer, but it achieved very high electrolysis efficiency (in high calorific value) exceeding 84% at best. We also obtained excellent results on the purity of the hydrogen gas produced in that the hydrogen gas contained less than 0.1 vol% oxygen (in dry base), verifying the high gas-separation ability of the diaphragm we developed.

Water electrolysis technologies are becoming more important for further promotion of renewable energy and establishment of a hydrogen-based society in the future. Kawasaki will continue to work on further improvement of durability and further cost reduction for key components such as electrodes and diaphragms, as well as studies on future commercialization.

Conclusion

Kawasaki believes that, through such technology development, we came to recognize what technologies were required to produce a large amount of inexpensive hydrogen and established the fundamental technologies for building a hydrogen energy supply chain in the future.

For the hydrogen production technologies by water electrolysis in the project in Hokkaido, we received tremendous support from NEDO, who commissioned the project, and co-implementers including Toyota Tsusho Corporation. We would like to sincerely thank everyone for their help.

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