Development of Compact Hydrogen Generator for On-site Hydrogen Station

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1. Introduction

Fuel Cell Vehicles ("FCV") powered by hydrogen are expected to be popularized as the ultimate eco cars that emit no CO_2 and air pollution in running. Japan plans to launch the sales of FCV production models in 2015 and provide about 100 hydrogen stations in advance. Now, hydrogen energy draws increasing attention as a key to realize the low-carbon society. The needs for development in hydrogen generation, storage and supply technologies also rise.

Osaka Gas Co., LTD. has focused attention on hydrogen as a next-generation clean energy while developing eco-friendly city gas appliances such as high-efficiency city gas cogeneration system and household fuel cell named "ENE-FARM". Osaka Gas has been developing hydrogen generators from Japanese city gas (calorific value is 45 MJ/m^{3}N) and studying on demonstration of a hydrogen station. From the first half of the '90s, Osaka Gas had sold 6 hydrogen generation units, called OGHH (Osaka Gas High-purity Hydrogen, see Fig.1), having the capacity of 100-1600 m^{3}N/h. Then, Osaka Gas has developed the compact and cost-effective hydrogen generators "HYSERVE[1)]" since the first half of the 2000s, and produced HYSERVE-30 having a capacity of 30 m^{3}N/h (Fig.2) and HYSERVE-100 having a capacity of 100 m^{3}N/h (Fig.3) on a commercial basis. As of August 2014, 16 units of the HYSERVEs were installed for industrial use and in hydrogen stations in Japan and abroad. Moreover, our new hydrogen generator for on-site hydrogen station, HYSERVE-300, having a capacity of 300 m^{3}N/h (Fig.4) and HYSERVE-100 which using LPG as a source gas (Fig.6) have been developed.

This paper describes the hydrogen generation process using city gas and the outline of HYSERVE. Also, the development and future efforts of HYSERVE-300 and LPG type HYSERVE-100, the hydrogen generator for on-site hydrogen station, are explained.

Fig. 1 OGHH

Fig. 2 HYSERVE-30

Fig. 3 HYSERVE-100

Fig. 4 HYSERVE-300

2. Outline of hydrogen generator

The hydrogen generator "HYSERVE" comprises a reforming part for generating hydrogen rich mixed gas from city gas and LPG by steam reforming reaction and a hydrogen refining part for deriving high-purity hydrogen from the mixed gas.

2.1.1 Desulfurization part

Feed gas compressed to about 0.9 MPaG is supplied to the reforming part. Before steam reforming, the sulfur component in feed gas must be removed to avoid the deterioration of reforming catalyst activity due to sulfur in gas. In desulfurization process (see the formula below), the sulfur in feed gas is converted to hydrogen sulfide via hydrodesulfurization reaction at 200 degrees C - 300 degrees C. Then, the sulfur component is removed by using desulfurization sorbent (ZnO) and superhigh-order desulfurizing agent. Osaka Gas uses a unique superhigh-order desulfurizing agent in HYSERVE and realizes the reduction of sulfur component in feed gas to ppb level.

[Hydrodesulfurization reaction]

$R\text{-}SH$ (mercaptan) + $H_2 \rightarrow RH + H_2S$ R=alkyl group

[Adsorptive desulfurization reaction]

$ZnO + H_2S \rightarrow ZnS + H_2O$

2.1.2. Steam reforming part

The desulfurized gas is mixed with steam and heated up to a certain temperature by a gas heating device, then supplied to a reformer. In the reformer, the reformed gas having hydrogen concentration approx. 70 vol% is generated via steam reforming reaction at 700 degrees C -800 degrees C (see the formula below). Osaka Gas uses a unique reforming catalyst for HYSERVE to realize high activity of steam reforming and reduce the risk of carbon deposition even if S/C ratio is low in feed gas.

[Steam reforming reaction]

$CH_4 + H_2O = 3\,H_2 + CO$ (Endothermic reaction)

2.1.3. CO shift conversion part

To increase hydrogen quantity in the reformed gas, the reaction between CO in the reformed gas and steam is induced by the CO shift converter. CO shift conversion reaction expressed as a formula below makes the reformed gas to have higher hydrogen concentration up to 75 vol%. Osaka Gas uses a unique low-temperature CO conversion catalyst in HYSERVE. This catalyst achieving higher temperature heat-resistance can be used in a wide range of temperature from 200 degrees C to 350 degrees C and be applied to CO shift conversion with just one catalyst. Additionally, this catalyst enables to reduce CO concentration in the reformed gas compared with a high-temperature CO conversion catalyst.

[CO shift conversion reaction]

$CO + H_2O = CO_2 + H_2$ (Exothermic reaction)

2.2.4 Hydrogen refining part

The reformed gas after CO shift conversion part is cooled to ambient temperature and proceeds to hydrogen refining process after separating excess water to drain off. In hydrogen refining part, impure substances such as H_2O, CO_2, CH_4 and CO are removed from the reformed gas by PSA (Pressure Swing Adsorption), and high-purity hydrogen is generated. The adsorbed impure substances are depressurized and washed, then exhausted as offgas. The refining procedure, adsorbing - desorbing - washing, are carried on in order at the 3 or 4 adsorption towers to obtain high-purity hydrogen continuously. Besides, the exhaust offgas is utilized as a fuel for burners of the reformer.

3. Features of compact hydrogen generator "HYSERVE"

The features of HYSERVE are described below:

(1) On-site hydrogen generation

High-purity hydrogen can be easily generated on site by using city gas supplied via pipeline.

(2) Compact design

The reforming part is compactly designed by adopting a compression type reformer so that HYSERVE realizes one of the world smallest unit sizes.

(3) Cost-effective

The production cost and the field construction cost are reduced by standardizing the system specifications and providing as an integrated package. Moreover, the compression power can be significantly reduced by utilizing city gas of medium pressure (>0.1MPaG) as a material gas.

(4) High efficiency

The offgas exhausted at hydrogen refining part contains flammable substances such as CH_4, CO and H_2. All of these flammable substances are recovered as a fuel for burners of the reformer to improve the efficiency of reforming process.

(5) Auto-operation

Using the automatic control program, hydrogen supply can start/stop safely and easily by touch panel operation. Also, the function for automatic load adjustment of hydrogen generation depending on hydrogen consumption is provided as a standard. Therefore, any specialized techniques are not necessary for operating HYSERVE. Additionally, an optional function, the remote monitoring system, enables that; data acquisition and monitoring from a distance; sending e-mail at an abnormal occurrence; unattended operation.

(6) Hot standby operation by hydrogen circulation

Generally, an on-site hydrogen generator is frequently stopped and started-up due to outside hours at nighttime in a hydrogen station in Japan. Cold start and stop operation may cause a machine trouble that the catalyst pulverized by thermal expansion/shrinkage of reformer reaction tube becomes a cause of obstruction. This trouble can be avoided by hot standby operation that keeps the temperature of hot area. HYSERVEs have the feature of hot standby operation as a standard that circulates hydrogen in reforming system based on the following ideas (Fig.5);

a. Shortening of start-up time: It will take much time to satisfy the quality of hydrogen production after start-up if nitrogen is circulated in standby operation because the hydrogen PSA is not meant for separate nitrogen from mixed gas.

b. Reduction of fuel consumption: HYSERVEs can operate hot standby operation by minimum quantity of fuel because the reforming part is heated up with burners using fuel only to compensate for the lost calories by circulated hydrogen cooling and equipment heat loss.

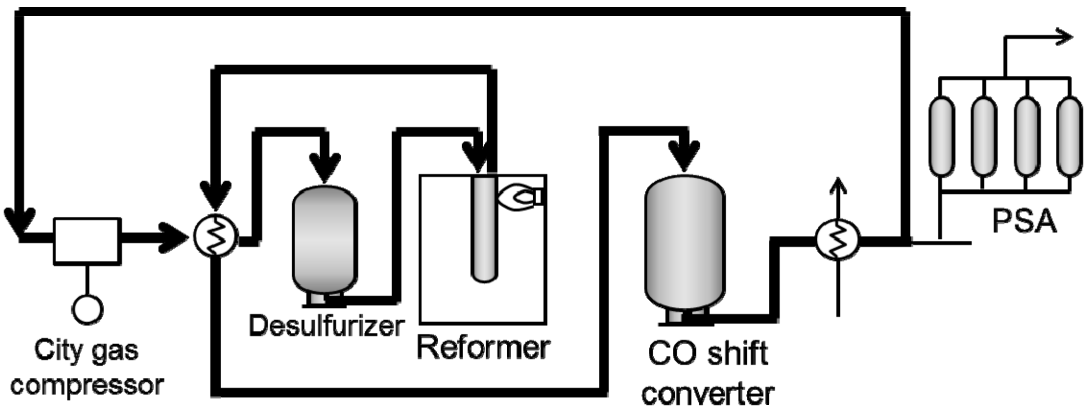

Fig. 5 Hydrogen circulation flow

4. Development of HYSERVE-300

4.1 Design concept and features

HYSERVE-300 achieved further improvement of reforming efficiency as well as taking over the design concept of conventional HYSERVE series that realizes cost effectiveness and compact design.

(1) Cost-effective and compact design

We scaled up the equipment and reconsidered the types of heat exchanger. Then, we achieved 50% of equipment cost reduction and 42% of space-saving for a HYSERVE-300 compared with 3 units of HYSERVE-100.

(2) High efficiency

We reviewed the hydrogen generation process and applied the following three improvements. Then, we achieved 11% of increase in reforming efficiency (= the ratio of calorific value of hydrogen product to the calorific value of consumed fuel) than conventional HYSERVEs.

a. Improvement of reformer furnace

We increased heat input to the reformer furnace tube and achieved 16% of increase in efficiency of reformer furnace (= the ratio of he calorific value used for reaction in the reformer furnace to the calorific value of consumed fuel in the reformer) according to the following improvements.

- Changing the type of burner
- Installing the radiation cylinder

b. Enhancement of waste heat recovery

We enhanced a function of waste heat recovery than conventional HYSERVEs and added the following heat exchangers.

- Combustion air preheater: recovering heat of combustion exhaust gas
- Pure water preheater: recovering heat of reformed gas from the outlet of CO shift converter

c. Applying the vacuum regeneration system PSA (VPSA)

We developed a VPSA system to improve hydrogen recovery rate (= the flow rate of total hydrogen product to the flow rate of hydrogen in mixed gas at the inlet of PSA). Regeneration of adsorbent is stimulated in PSA by depressurizing with using a vacuum pump. Then, the hydrogen recovery rate is improved to 85% from the conventional approx.74%.

Table 1 shows the specifications of HYSERVE-30, HYSERVE-100 and HYSERVE-300.

Table 1: Specifications of HYSERVE series

Model	HYSERVE-30	HYSERVE-100	HYSERVE-300
H_2 generation capacity	30 m^3N /h	100 m^3N /h	300 m^3N /h
Material	Japanese city gas[*1] LPG	Japanese city gas[*1]	Japanese city gas[*1]
Purity of H_2	More than 99.999 vol%	More than 99.999 vol%	More than 99.999 vol%
Basic unit[*2]	0.42 m^3N-raw/ m^3N -product	0.40 m^3N -raw/ m^3N -product	0.36 m^3N -raw/ m^3N -product
Pressure of H_2 product	Less than 0.70 MPaG	Less than 0.70 MPaG	Less than 0.70 MPaG

[*1]: Calorific value: 45MJ/m^3N

[*2]: The ratio of flow rate of Japanese city gas (45MJ/m^3N) to the flow rate of product hydrogen.

5. Development of LPG type HYSERVE-100

Osaka Gas has also developed another HYSERVEs using LPG (supposed composition; C_2H_6 1%, C_3H_8 98%, C_4H_{10} 1%). We revised the process balance of HYSERVE because the feed gas composition, heat-transfer property changed. And we also revised the design of PSA because the flow rate of impure substance in reforming gas increased. Osaka Gas has announced to commercialize LPG type HYSERVE-30 in 2004. And Osaka Gas developed LPG type HYSERVE-100 (Fig.6) in 2014. One LPG type HYSERVE-30 has already installed and been operating stably up to the present date. Osaka Gas plans to develop the LPG type HYSERVE-300 hereafter.

Fig. 6 LPG type HYSERVE-100

6. Demonstration unit

During the development of HYSERVE-300 and LPG type HYSERVE-100, we produced a demonstration unit (Fig.4, Fig.6) having the same hydrogen generation capacity (300 m^3N /h, 100m^3N/h) as a commercial unit. Table 2 and Table 3 show the required specification of hydrogen product to be generated by HYSERVE-300 and LPG type HYSERVE-100, and the result of demonstration testing. As shown in the excellent result of the demonstration, the hydrogen generator HYSERVE-300 and LPG type HYSERVE-100 have achieved the performance upgrade to satisfy the quality of hydrogen product aiming to supply hydrogen to FCVs.

Based on this development, Osaka Gas announced that they started to produce HYSERVE-300 on a commercial basis at the end of October in 2013.And Osaka Gas also announced that they started to produce HYSERVE-100 on a commercial basis at the end of March in 2014.

Table 2: HYSERVE-300 - Characteristics of hydrogen product

Item		HYSERVE-300 H_2 product (Specifications)	Actual result of demonstration testing
Flow rate of H_2 product		300 m^3N /h	305.2 m^3N /h
Purity of H_2 product		> 99.999 vol. %	> 99.9995 vol. %
Impurity concentration	CO	< 0.2 ppm	< 0.1 ppm
	CO_2	< 1.0 ppm	N.D. *3
	CH_4	< 1.0 ppm	N.D. *3
	N_2	< 10 ppm	< 2.0 ppm
	O_2	< 0.5 ppm	N.D. *4
Atmospheric dew point		< -80 ℃	< -90 ℃
Pressure of H_2 product		> 0.70 MPaG	> 0.70 MPaG

*3: lower detection limit 0.01ppm, *4: lower detection limit 0.1ppm

Table 3: LPG type HYSERVE-100 - Characteristics of hydrogen product

Item		HYSERVE-100 H_2 product (Specifications)	Actual result of demonstration testing
Flow rate of H_2 product		100 m^3N /h	101.5 m^3N /h
Purity of H_2 product		> 99.999 vol. %	> 99.9999 vol. %
Impurity concentration	CO	< 0.2 ppm	N.D. *3
	CO_2	< 1.0 ppm	N.D. *3
	CH_4	< 1.0 ppm	N.D. *3
	N_2	< 10 ppm	N.D. *3
	O_2	< 0.5 ppm	N.D. *4
Atmospheric dew point		< -80 ℃	< -80 ℃
Pressure of H_2 product		Less than 0.70 MPaG	Less than 0.70 MPaG

*3: lower detection limit 0.01ppm, *4: lower detection limit 0.1ppm

7. Future efforts

Osaka Gas contributes toward establishing the low-carbon society through the efforts to introduce and install HYSERVE-300 to hydrogen stations, and also promotes the installation of HYSERVE-300 to medium-scale industrial user's sites in Japan and abroad, too.

Osaka Gas is also preparing to acquire the international standard ISO and IEC for HYSERVE to advance into foreign market. Regarding explosion-proof, HYSERVEs have satisfied the Japanese standard TIIS, however the acquisition of the international explosion-proof certification IECEx is now under consideration.

Besides, cost reduction, downsizing and high efficiency are also important to promote the construction of hydrogen stations. We will make further efforts to improve HYSERVE-300.

Reference

1) T. Asakura, et al., "Development of New Compact Hydrogen Production Systems from Natural Gas", Proceedings of 15th world Hydrogen Energy Conference, June (2004)