

## **Distributed Systems for Hydrogen Production from City Gas Combined with CO<sub>2</sub> Sequestration**

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### **1. INTRODUCTION**

Concerns about global warming have led to worldwide efforts to reduce CO<sub>2</sub> emissions in various fields and industrial sectors to create a low carbon society. Hydrogen, with its superiority in environmental compatibility and energy security, is attracting attention as an energy carrier that could play an important role in achieving a low carbon society. Indeed, work is underway on enabling hydrogen and fuel cells to be used in practice, particularly in the residential/commercial sector and transport sector where CO<sub>2</sub> emissions are increasing [1]. As stationary fuel cells and fuel cell vehicles become more practical and start to spread, the demand for hydrogen is expected to go beyond the existing demand for industrial use, as demand for hydrogen as a fuel will grow in the residential/commercial sector and the transport sector. Although hydrogen can be produced from a wide variety of raw materials, its widespread use requires the construction of highly efficient and reliable hydrogen supply infrastructure. Therefore, distributed systems for producing hydrogen onsite from city gas, based on existing networks for city gas distribution, are one of the most promising methods of producing hydrogen.

At Tokyo Gas, in addition to developing technologies for home-installed fuel cells, we have developed technologies for efficiently producing hydrogen from city gas at hydrogen stations in anticipation of fuel cell vehicles coming on the market. Building upon our earlier experience in developing hydrogen generators based on the conventional steam methane reforming (SMR) method and pressure swing absorption (PSA) method, we have been developing membrane reformers (MRFs) for efficiently producing/separating pure hydrogen by using membrane-based separation techniques. Figure 1 illustrates the operating principle of MRF. The MRF has a reformer that contains a hydrogen separating module (with a palladium alloy membrane for separating hydrogen) and catalyst. The membrane facilitates the production of pure hydrogen by separating and refining hydrogen in the reformed gas, thus enabling hydrogen to be produced by a single-stage process. Thanks to this advantage, a hydrogen generator based on this method is simpler, more efficient and more compact than a conventional hydrogen generator with SMR and PSA combined. While the conventional reformer requires a high temperature of 700–800°C to obtain

a high conversion ratio through chemical equilibrium, the MRF can produce a similar amount of hydrogen at 500–550°C through selective extraction of hydrogen from the reforming reaction unit by the separating membrane, thus leading the steam reforming reaction and the shift conversion reaction of CO toward increased production of hydrogen. A lower reaction temperature saves energy required for heating the reformer, while higher efficiency is also achieved by reducing the loss of energy by radiation, etc. Since the acceleration of reactions by the hydrogen separating membrane results in a higher concentration of CO<sub>2</sub> in the process gas, the off-gas from the reformer contains highly concentrated CO<sub>2</sub>.

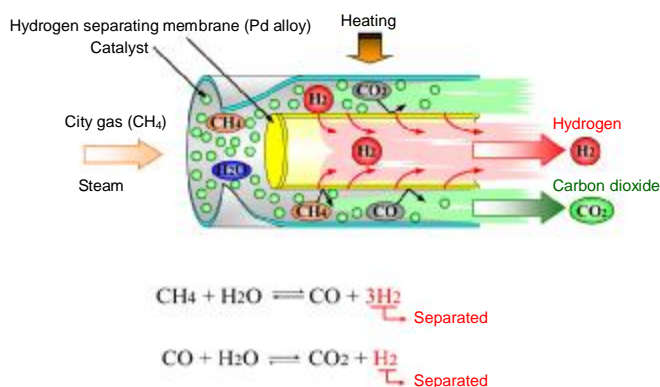


Figure 1. Configuration of MRF

## 2. PERFORMANCE OF A 40 Nm<sup>3</sup>/h-CLASS MRF

To create distributed systems for efficiently producing hydrogen from city gas, Tokyo Gas, as a member of the Japan Gas Association (JGA), worked on technologies for deploying such systems, addressing themes such improving the performance of the hydrogen separating membrane module and optimizing the reformer configuration, as part of activities led by the New Energy and Industrial Technology Development Organization (NEDO) from 2000 to 2004. For technological demonstration tests at hydrogen stations, we developed a prototype of 40 Nm<sup>3</sup>/h-class reformers

(our early MRF model), which successfully achieved in 2004 the energy efficiency of 76.2% (HHV) (= *energy of produced hydrogen / (energy of city gas fed into the reformer + electric power consumed by auxiliary components)*) [2]. We successfully made the system approximately three times smaller than the conventional reformer (SMR/PSA combination type), demonstrating the advantage of MRF in terms of compactness. From 2005, we worked on improving the hydrogen separating membrane module to raise higher efficiency and durability as part of a project led by NEDO for developing core technologies for safe utilization of hydrogen, etc. An improved version of our 40 Nm<sup>3</sup>/h-class prototype reformer (our improved MRF model) successfully achieved the world's highest energy efficiency of 81.4% (HHV) in producing hydrogen from natural gas. Since the energy efficiency in hydrogen production used to be 65–70% (HHV) with a conventional reformer (SMR/PSA combination type), our MRF outperformed it by as many as 10–15 points. Data from testing the 40 Nm<sup>3</sup>/h-class reformer has shown that the concentration of CO<sub>2</sub> in the off-gas from the MRF's reformer unit was as high as 70–90%. With such a high concentration, it may be possible to achieve CO<sub>2</sub> sequestration without requiring the usual concentration and absorption processes, and relying solely upon compression and vapor/liquid separation with lesser energy consumption.

## 3. DEMONSTRATION OF CO<sub>2</sub> SEQUESTRATION AT DISTRIBUTED SYSTEMS FOR HYDROGEN PRODUCTION

Figure 2 shows the breakdown of CO<sub>2</sub> emissions after the sequestration of highly concentrated CO<sub>2</sub> from the off-gas and the estimated CO<sub>2</sub> emission reduction ratio. The calculation was performed using operating data from our earlier MRF model. It was assumed that the off-gas was pressurized

using a compressor to at least 7 MPa and 29°C before being cooled to room temperature, and then all CO<sub>2</sub> in the off-gas was removed by a vapor/liquid separation tank. In estimating CO<sub>2</sub> emissions caused by electric power consumption, we assumed the CO<sub>2</sub> emission intensity of 0.339 kg/kWh (reported by Tokyo Electric Power for 2006). CO<sub>2</sub> sequestration solely by means of vapor/liquid separation is difficult for the off-gas from burners and boilers because the concentration of CO<sub>2</sub> in such combustion off-gas is too low. CO<sub>2</sub> emissions caused by electric power consumption cannot be captured at the customer's site. Therefore, the reformer off-gas provides the only opportunity for the sequestration of CO<sub>2</sub> by compression and vapor/liquid separation. Figure 2 demonstrates the feasibility of reducing CO<sub>2</sub> emissions by 46–58% using this method when the city gas feed rate is 3.2–11.6 Nm<sup>3</sup>/h. When the MRF is operating at 100% of the rated output (producing hydrogen at the rate of 40 Nm<sup>3</sup>/h), the estimated off-gas derived CO<sub>2</sub> reduction ratio is 55%.

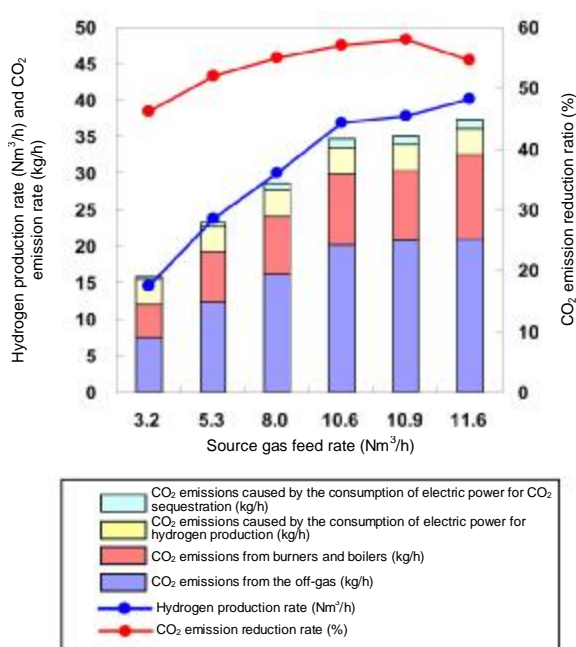


Figure 2 Breakdown of CO<sub>2</sub> emissions and the CO<sub>2</sub> emission reduction ratio

Table 1 Energy efficiency in hydrogen production and the CO<sub>2</sub> emission reduction rate

		MRF operating at 75% of the rated output (standalone)	MRF operating at 75% of the rated output (combined with CO <sub>2</sub> sequestration)
Energy input (MJ/kg-H <sub>2</sub> )	City gas	168.5	168.5
	Electricity	6.6	13.6
Hydrogen production rate (Nm <sup>3</sup> /h)		30.6	30.6
Overall efficiency (% , HHV) *1		81.7	78.6
CO <sub>2</sub> emission rate (kg/h)		25.1	12.6
CO <sub>2</sub> emissions reduction rate (%)		-	50

\*1: The electric power consumed by the hydrogen compression/absorption unit is excluded from the calculation of the overall efficiency.

\*2: The CO<sub>2</sub> emission intensity of 0.339 kg/kWh (reported by Tokyo Electric Power for 2006) is assumed in the calculation of CO<sub>2</sub> emissions caused by the consumption of electric power.

For demonstrating on a real machine the performance of a distributed system for efficiently producing hydrogen from city gas combined with CO<sub>2</sub> sequestration, we produced a 1 Nm<sup>3</sup>/h-class CO<sub>2</sub> sequestration unit and combined it with our improved 40 Nm<sup>3</sup>/h-class MRF for a demonstration test. Figure 3 shows the appearance of the tested equipment. The CO<sub>2</sub> sequestration unit comprised a moisture absorption column, compressor, heat exchanger, chiller, vapor/liquid separation tank and CO<sub>2</sub> storage tank. A part of the off-gas was fed into the CO<sub>2</sub> sequestration unit, and we measured the amount of CO<sub>2</sub> separated into the storage tank. Table 1 shows the energy efficiency in hydrogen production and the CO<sub>2</sub> emission reduction rate when the MRF operates at 75% of the rated output (hydrogen production rate of 30.6 Nm<sup>3</sup>/h and CO<sub>2</sub> concentration in the off-gas of 81.7%), as values estimated from the demonstration test results. The consumption of electric power by CO<sub>2</sub> sequestration increased the energy input by 7.0 MJ per kilogram of hydrogen produced. The energy efficiency was 81.7% (HHV) when hydrogen is produced without CO<sub>2</sub> sequestration. The energy efficiency dropped to 78.6% (HHV) when hydrogen production was combined with CO<sub>2</sub> sequestration. Thus, the drop in energy efficiency was as little as 3.1 points. The 91.5% of CO<sub>2</sub> was removed from the off-gas and the CO<sub>2</sub> sequestration reduced CO<sub>2</sub> emissions from

25.1 kg/h to 12.6 kg/h, which translates into a reduction ratio of 50%.



Figure 3 Appearance of 40 Nm<sup>3</sup>/h-class MRF combined with CO<sub>2</sub> sequestration unit

#### 4. CONCLUSION

We conducted the world's first demonstration test of a distributed system for producing hydrogen from city gas combined with CO<sub>2</sub> sequestration and showed that CO<sub>2</sub> sequestration could halve CO<sub>2</sub> emissions while limiting the reduction of energy efficiency to approximately 3%. This confirmed the feasibility of CO<sub>2</sub> sequestration even at a small distributed system for hydrogen production. The MRF, when combined with CO<sub>2</sub> sequestration, will allow hydrogen to be efficiently produced from city gas with lower CO<sub>2</sub> emissions even when the hydrogen is produced using distributed systems. This technology is expected to provide a promising option for the natural gas industry in support of a low carbon society of the future.

#### Acknowledgement

We conducted research and development on the MRF under consignment from the New Energy and Industrial Technology Development Organization (NEDO). We sincerely thank all those who assisted us in this project.

#### References:

- [1] *Annual Report on the Environment and the Sound Material-Cycle Society in Japan 2007*, Ministry of the Environment
- [2] Yoshinori Shirasaki and Isamu Yasuda, *Hydrogen Energy System*, Vol. 31, No. 2, p. 43 (2006) [in Japanese]