Development of a Nuclear Hydrogen Production System by Dimethyl Ether (DME) Steam Reforming and Related Technology*

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Abstract
Targeting a hydrogen production system using heat produced by a nuclear reactor at about 300 °C, we are developing a dimethyl ether (DME) steam reformer and hydrogen purification systems as well as catalysts for DME reforming. The use of heat from a nuclear reactor suppresses the CO₂ concentration change in the atmosphere. In our developments, a catalyst, consisting of mixed oxides, produced hydrogen at a rate of about 1.9 Nm³/h per catalyst volume (m³) at about 300 °C. Subsequently, the DME steam reformer achieved a hydrogen production rate of approximately, at least, 1.4 Nm³/h at about 300 °C, by absorbing heat from the supplied steam. The aforementioned hydrogen production system via DME steam reforming is to be demonstrated using a thermal power plant. DME steam reforming by using waste heat and the utilization of the produced hydrogen within a combined cycle power plant can reduce fuel consumption, for instance, by about 17% compared to the case of direct DME combustion. The total system, with the use of DME, was compared with the methane case. If necessary, the byproduced CO₂ may be injected into coal seams, increasing CH₄ production via the substitution of CO₂ for CH₄ on coal, where CO₂ adsorption is expected to be stronger than the CH₄ adsorption.

Key words: Nuclear Hydrogen Production, DME, Steam Reforming, Low Temperature, CO₂ Sequestration

1. Introduction
This paper reports concerning the development of a nuclear hydrogen production system via dimethyl ether (DME) steam reforming, which uses heat at low temperatures of about 300 °C from a nuclear reactor. There are certain purposes for the low temperature nuclear hydrogen production system, one of which is the multipurpose use of a nuclear reactor. At present, nuclear energy is used only in the form of electricity converted from heat, but the nuclear hydrogen production system produces hydrogen, which has the potential for use in a variety of fields. In the case of the methane steam reforming for hydrogen production, operating temperatures are about 500-900 °C and the system requires a high-temperature gas-cooled reactor or a fast-breeder reactor. On the other hand, the hydrogen production system using DME steam reforming, with
operating temperatures of around 300 °C, makes it possible to use a light water reactor or a fast breeder reactor. By using the produced hydrogen to generate power, it will become possible to store energy in the form of hydrogen energy and convert the latter to electric power according to the load change. Hydrogen may also be supplied to city gas systems, to hydrogen stations for internal-combustion engine cars and fuel cell vehicles, as well as to stationary fuel cells such as those at home. The use of hydrogen helps limit air pollution. Since the DME steam reforming involves an endothermic reaction, the utilization of hydrogen whose energy is elevated by the heat absorption compared to DME will suppress the change in the level of CO₂ concentration in the atmosphere. It is probably the safest way to maintain the present global environmental level from the viewpoint of the global environment. CO₂ which is byproduced during the DME steam reforming may be injected into coal seams if necessary, which increases the methane production from the latter. Concerning CO₂ sequestration into the ground or under the sea bed, the IPCC meeting held in Montreal in September, 2005 adopted the special report presented. Furthermore, the London protocol was amended and CO₂ sequestration was internationally approved. In Japan, targeting practical use in 2020, the CCS2020 project has started.

We reported the concept of a hydrogen production system via DME steam reforming in the previous ICONE11 held in Tokyo. Since ICONE11, we have developed catalysts for the DME steam reforming, steam reformers to produce hydrogen by supplying heat as well as a hydrogen purification system removing CO and CO₂ from the hydrogen gases produced. The present authors have a plan to demonstrate the hydrogen production system via DME reforming in a thermal power plant, before the practical application of the hydrogen production plant with a nuclear reactor. This paper reports on our development after ICONE11.

This paper is organized as follows: Section 2 is devoted to report on our development of the DME steam reformer, while in Section 3, the hydrogen production system via DME reforming will be presented, followed by a DME cycle given in Section 4. Finally, Section 5 will summarize conclusions.

Nomenclature

\[ \Delta H_f: \] change of enthalpy in the DME steam reforming reaction
\[ \Delta H_{f25}(A): \] energy of formation per unit mol of material A at 25 °C

Subscripts

\( f \): formation
\( f25 \): formation at 25 °C

2. Development of a DME Steam Reformer for Hydrogen Production

Figure 1 is a schematic diagram of a hydrogen production process via DME steam reforming. The DME is reformed at temperatures of about 300 °C, expressed by an endothermic reaction as

\[ \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2 \quad -122.59 \text{ kJ}. \]  

Here, the change in standard enthalpy (per mol) in the DME steam reforming reaction is

\[ \Delta H_f = 6\Delta H_{f25}(\text{H}_2) + 2\Delta H_{f25}(\text{CO}_2) - \Delta H_{f25}(\text{CH}_3\text{OCH}_3) - 3\Delta H_{f25}(\text{H}_2\text{O}), \]  

\[ (1) \]
where

\[ \Delta H_{f25}(A) \]: the energy of formation per unit mol of material A at 25°C.

The values of \( \Delta H_{f25} \) for CH\(_3\)OCH\(_3\), H\(_2\)O, CO\(_2\), CH\(_3\)OH, CH\(_4\), O\(_2\) and CO are -184.1, -241.83, 0, -393.5, -201, -74.87, 0 and -110.53 kJ/mol, respectively\(^{(5)}\). When the methane reforming uses city gas, desulfurization is necessary due to the added sulfur unlike in DME reforming. The reaction of the DME steam reforming is composed of an elementary reaction

\[
\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} - 23.93 \text{ kJ},
\]

(3)

Fig. 1  Schematic diagram of a hydrogen production process via DME (dimethyl ether) steam reforming

which transforms DME to methanol, and the following methanol steam reforming reaction

\[
2\text{CH}_3\text{OH} + 2\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2 - 98.66 \text{ kJ},
\]

(4)

which produces hydrogen.

Fig. 2  Hydrogen formation fraction derived by thermodynamic equilibrium analysis
Thermodynamic equilibrium analysis shows that the hydrogen formation fraction becomes like Fig. 2 when methane is not byproduced. The ratio of steam and DME was 3:1 (DME:H₂ was 1:6). In Fig. 2, the calculated line for 1 atm almost coincides with that for 2 atm and does not deviate significantly. The result shows that at a temperature of 300 °C, the hydrogen production fraction is high. In actual fact, the transformation of DME to methanol is promoted using a solid acid catalyst like Al containing oxide as shown in Fig. 3. The subsequent hydrogen production reaction via methanol steam reforming is advanced using a metal catalyst such as Cu (with added Zn) in the surface of the oxide ceramics.

A hydrogen production test was performed by using an equipment, whereby the

![Fig. 3 Catalyst for the DME reforming processes](image)

![Fig. 4 Experimental equipment for hydrogen production via DME steam reforming](image)

![Fig. 5 DME conversion fraction achieved experimentally](image)
reformer was filled with the aforementioned catalyst, shown in Fig. 4. DME gas mixed with vapor and preheated enters the reformer and then reacts with steam with the help of catalysis. The heat necessary for an endothermic reaction via DME steam reforming was supplied through steam heated by the boiler. Figure 5 shows the experimental DME conversion fraction by steam heating, where experimental results involving smaller equipment with the use of the electric heating are also shown. The condition in the steam heating test was as follows. The catalyst was immobilized on the surface of a medium with a 3-dimensional network structure. The medium was made of ceramics, of which the main component was alumina. Two catalyst-immobilized mediums of diameter around 15 mm and height around 20 mm were packed into a reactor tube of inner diameter 16.5 mm and height of 100 mm. The DME feed rate was 30 Ncm$^3$/min and the ratio of steam and DME was 5. The operating pressure was atmospheric pressure and the contents of the gas were analyzed with a gas chromatograph.

The condition in the smaller equipment with the electric heating was as follows. The catalyst shape was the same as that used in the steam heating test. Fifteen catalyst-immobilized mediums of diameter around 50 mm and height around 50 mm were packed into a reactor tube of inner diameter 54.9 mm and height 1000 mm. The DME feed rate was 150 Ncm$^3$/min and the ratio of steam and DME was 5. The operating pressure was atmospheric pressure. The contents of the gas were analyzed with a gas chromatograph. The DME conversion fraction was almost 100 % at a temperature of 300 ºC.

Figure 6 shows the experimental hydrogen production rate per 1m$^3$ of catalyst volume as a function of the temperature and the hydrogen production rate was 1.9 Nm$^3$/h at 300ºC. The test condition of obtaining data in Fig. 6 was as follows. The catalyst was prepared by compressing the mixture of the powder of Cu-Zn catalyst and zeolite ZSM-5. The size of the compressed medium was about 3 mm. 5.2 cm$^3$ in volume of the compressed medium were packed into a reactor tube of inner diameter 21 mm and height of 300 mm. The DME feed rate was 30 Ncm$^3$/min and the ratio of steam and DME was 5. The operating pressure was atmospheric pressure. The contents of the gas were analyzed with a gas chromatograph. Next a scale-up test was carried out, where 740 cm$^3$ of the same catalyst medium were packed into a reactor tube of inner diameter 22.2 mm and height of 300 mm. The DME feed rate was 4700 Ncm$^3$/min and the ratio of steam and DME was 5. The operating pressure was atmospheric pressure. The contents of the gas were analyzed with a gas chromatograph. The total hydrogen production rate achieved was about 1.4 Nm$^3$/h at 300 ºC.

![Hydrogen production rate achieved experimentally via DME steam reforming](image)

**Fig. 6** Hydrogen production rate achieved experimentally via DME steam reforming

### 3. Hydrogen Production System via DME Steam Reforming

A schematic diagram of a nuclear hydrogen production system via DME steam reforming...
reforming is shown in Fig. 7. This hydrogen production system can use heat at about 300 °C from the light water reactor as well as a fast breeder reactor. The DME and water fed are preheated and mixed before entering the DFM reformer and heated in the reformer by steam from the nuclear reactor. The produced hydrogen is separated by a pressure swing adsorption system and is sent to hydrogen storage systems and utilization systems.

Fig. 7 Schematic diagram of a nuclear hydrogen production system via DME steam reforming

Since 122.59 kJ is absorbed by one mole of DME producing 6 mol of H₂ during the DME steam reforming, 10 MW/year=2.52×10⁸ MJ (with 80 % operating efficiency) of heat yields 2.772×10⁸ Nm³. It is noted that the hydrogen needed for 5 million fuel cell vehicles is estimated to be about 3,000 MNm³/yaer, which is as much as 10 times or so the aforementioned level. With the use of nuclear hydrogen production, the fraction of nuclear energy may be raised, whereby excess nuclear power is stored in the form of hydrogen energy, and upon demand, power may be, for instance, supplied by hydrogen gas turbines with steam turbines.

The authors plan to demonstrate the hydrogen production system via DME reforming in a thermal power plant before installing a hydrogen production plant in a nuclear reactor. The heat of the steam and the exhaust gas from the power plant can be used for the demonstration. In addition, as a preliminary step before the upcoming practical use of the DME reformer in a nuclear reactor, it is expected that the DME reformer will be installed with the hydrogen turbine combined cycle power plant at garbage incineration sites and ironworks as shown in Fig. 8. The analyzed result indicates that 17 % of DME fuel can be saved compared to the simple DME combustion case. In Europe, plans for an addition of

Fig. 8 Systems of hydrogen production via DME steam reforming and utilization of the produced hydrogen
about 10% of hydrogen to natural gas pipelines are progressing. There is also the potential for hydrogen to be added to city gas systems. Hydrogen can, of course, be supplied to hydrogen stations for internal-combustion engine cars and fuel cell vehicles, as well as to stationary fuel cells such as those at home.

In considering the steam reforming system and with the hydrogen turbines shown in Fig. 8, we note that the DME reforming system operates with a heat supplying system at about 300 °C, while the methane reforming system requires a heat supplying system at about (500-) 900 °C. With this in mind, heat supplied to the DME reformer cannot be supplied to the methane reformer from a water cooled nuclear reactor. We hereby carry out a rough estimation. The higher heating values (hhv) for DME, methane and hydrogen are 1496, 1777 and 571 kJ/mol, respectively\(^6\). One DME molecule corresponds to roughly two (strictly 1.7) methane molecules and the steam reforming for one DME molecule and two methane molecules produces six and eight hydrogen molecules, respectively. The hydrogen gas produced by DME reforming has higher energy than DME, while the energy gain in the methane reforming case is about twice that in the DME case.

4. An Expected Plan of the DME Cycle

CO\(_2\) which is byproduced during the DME steam reforming may be injected into coal seams if necessary, which increases the methane production from coal seams as shown in Fig. 9. CO\(_2\) injected in coal seams releases methane via pressure and by the substitution of CO\(_2\) for methane. It is thought that the CO\(_2\) substitution for methane is caused by the stronger bond of CO\(_2\) with the coal surface compared to the corresponding bond of CH\(_4\). Liquefying the methane produced from coal seams is not easy, but it is possible to synthesize DME from methane for transportation. When partial oxidation is used for the DME synthesis from methane, the whole reaction is exothermic as follows and CO\(_2\) is not emitted.

\[
2\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} + 276.19 \text{ kJ}. \tag{5}
\]

The whole reaction for the DME synthesis is composed of many elementary reactions, and appropriate employment of the reactions can utilize CO\(_2\).

\[
\frac{1}{3}\text{CH}_4 + \left(\frac{2}{3}\right)\text{O}_2 \rightarrow \frac{1}{3}\text{CO}_2 + \left(\frac{2}{3}\right)\text{H}_2\text{O} + 267.43 \text{ kJ}, \tag{6}
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 - 206.17 \text{ kJ}, \tag{7}
\]

\[
\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_2\text{OH} + 90.47 \text{ kJ}, \tag{8}
\]

\[
\frac{1}{3}\text{CO}_2 + \text{H}_2 \rightarrow \frac{1}{3}\text{CH}_3\text{OH} + \frac{1}{3}\text{H}_2\text{O} + 16.44 \text{ kJ}, \tag{9}
\]

\[
\frac{4}{3}\text{CH}_2\text{OH} \rightarrow 2\left(\frac{2}{3}\right)\text{CH}_3\text{OCH}_3 + \left(\frac{2}{3}\right)\text{H}_2\text{O} - 306.49 \text{ kJ}. \tag{10}
\]

CO\(_2\) reforming of CH\(_4\), which is expressed by

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 - 247.31 \text{ kJ}, \tag{11}
\]

also uses CO\(_2\). Biomass such as methane is also available as raw materials for DME synthesis.

During the DME synthesis expressed by Eq. (5), the energy loss of DME is 276.19 kJ/mol, while, the process compressing methane to produce LNG requires 20.5 kJ/mol\(^7\).
Since the ratio of the heating value of DME and that of methane is 1:1.7, the synthesis energy of DME is 8.17 times the compression energy of methane. However, due to the 0.6th power rule relationship between the cost and the plant size, an LNG plant loses superiority when the plant is built in a small gas field and the plant size is reduced to be 1/35 times that of the large plant. Since DME plants are available even to the small gas field, the DME plants are economically compatible with LNG plants in this filed case. Furthermore, the boiling point of DME, which is -25 °C, is higher than that of LNG, which is -162 °C.

For DME transportation, DME needs to be cooled down to about -25 °C, but when CO₂ is transported by ship, which is to be used for DME transportation, DME can be cooled by exchanging heat between cooled CO₂ and DME. As for the CO₂ sequestration into the ground or under the sea bed, the IPCC meeting held in Montreal in September, 2005 adopted the special report presented. Moreover, the London Protocol was amended and CO₂ injection into sub-sea bed geological formations was internationally approved. In Japan, targeting practical use in 2020, the CCS2020 project is underway. This project includes CO₂ separation during the fuel pre-reforming process for a hydrogen turbine combined cycle, and CO₂ sequestration. A company in the UK and a U.S. counterpart are jointly preparing two projects in the North Sea and California, each with respective investment of about 1,000 million US$, respectively, where oil is reformed to have low viscosity and oil production is increased via CO₂ injection into oil fields.

According to RITE (Japan) data for CO₂ sequestration, the fraction of the pressurizing cost for injection relative to the total CO₂ sequestration cost is about 1/4 and the pressurizing energy is estimated to be approximately 7.8-9.1 kJ/DME-mol.

![Fig. 9 Schematic diagram for an expected plan of the DME cycle](image)

### 5. Conclusions

As reported in this paper, the present authors are developing a dimethyl ether (DME) steam reformer and hydrogen purification systems as well as catalysts for DME reforming for the hydrogen production system using heat produced by a nuclear reactor at about 300 °C. The use of heat from a nuclear reactor contributes to maintaining the present CO₂ density in the atmosphere. Our catalyst, which consist of mixed oxides, produced hydrogen at a rate of about 1.9 Nm³/h per catalyst volume (m³) at about 300 °C. Subsequently, the DME steam reformer achieved a hydrogen production rate of approximately, at least, 1.4 Nm³/h at a temperature of about 300 °C, by absorbing heat from the supplied steam.

The hydrogen production system via DME reforming will be demonstrated using a thermal power plant. DME steam reforming by using waste heat and the utilization of the produced hydrogen in a combined cycle power plant can save fuel, for instance, by about...
17% compared to the direct DME combustion case. The total system, with the use of DME, was compared with the methane case. If necessary, byproduced CO₂ may be injected into coal seams, resulting in an increasing in CH₄ production by the substitution of CO₂ for CH₄ on coal, whereby CO₂ adsorption is expected to be stronger than the CH₄ case.

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