Conceptual Design of a Hydrogen Production System by DME Steam Reforming and High-Efficiency Nuclear Reactor Technology

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Hydrogen is a potential alternative energy source and produced commercially by methane (natural gas) or LPG steam reforming, a process that requires high temperatures, which are produced by burning fossil fuels. However, since this process emits large amounts of CO₂, replacement of the combustion heat source with a nuclear heat source for 773-1173 K processes has been proposed in order to eliminate these CO₂ emissions. This paper proposes a novel method of low-temperature nuclear hydrogen production by reforming dimethyl ether (DME) with steam produced by a low-temperature nuclear reactor at about 573 K. The authors identified conditions that provide high hydrogen production fraction at low pressure and temperatures of about 523-573 K. By setting this low-temperature hydrogen production process at about 573 K upstream from a turbine, it was found theoretically that the total energy utilization efficiency is about 50% and very high. By setting a turbine upstream of the hydrogen production plant, an overall efficiency of is 75% for an FBR and 76% for a supercritical-water cooled power reactor (SCPR).

KEYWORDS: low-temperature nuclear hydrogen production, dimethyl ether (DME), steam reforming, low-temperature nuclear reactors, FBR, SCPR, hydrogen production fraction, energy-utilization efficiency

I. Introduction

It is recognized that the average global temperature will rise by about 3 K due to CO₂ emissions by 2100. The development of fuel cells for vehicles, which are environmentally sound power sources, has become an important field of research. The Japan government has a plan to reduce CO₂ emissions by replacing 5 million gasoline-powered vehicles by fuel cell powered vehicles by 2020. Then, the demand for hydrogen will become 40 giga Nm³/year by 2020. Commercially, hydrogen is produced by methane (natural gas) or LPG steam reforming at about 1173 K produced by burning fossil fuels. However, this process emits large amounts of CO₂, and it is proposed that the combustion heat sources should be replaced by nuclear heat source for high-temperature (about 1133 K) process or medium temperature (about 773K) process in order to eliminate these CO₂ emissions.¹,² These two steam reforming processes are effective for supplying hydrogen, but the operating temperature is still too high for the use of low-temperature nuclear reactors.

The authors, then, present a novel method of low-temperature nuclear hydrogen production by reforming dimethyl ether (DME) with steam produced by a low-temperature nuclear reactor at about 573 K.³ The DME steam reforming at low temperatures can use a low-temperature nuclear reactor as a heat. Since the hydrogen production system is free from desulfurization and primary CO transformation, the system becomes simple and compact. DME is transported by an LPG ship (or a slightly modified LPG ship), because DME is liquefied by compression without cooling. Consequently, C.I.F. (cost, insurance, and freight) for DME is expected to be cheaper than that for LPG. In the press, several industrial groups have announced that transportation of DME to Japan will begin around 2006. In addition, there is a possibility that light oil, which is used for diesel automobiles but produces carcinogenic black smoke when it burns, may be replaced by DME.

According to thermodynamic equilibrium analysis, it was found that the hydrogen production fraction is high at about 573 K. Then, the equilibrium mass and heat balance analysis for a nuclear reactor with an installed DME hydrogen production system showed that the total energy utilization efficiency is about 53 %; 30 % for the hydrogen production system and 23 % for the turbine for the case of a nuclear reactor with about 573 K coolant (the hydrogen production process is set upstream from a turbine). Whereas, an overall efficiency is about 75 %; 49 % for the hydrogen production system and 26 % for the turbine for the case of a fast breeder reactor with about 773 K coolant (the hydrogen production process is set downstream of a turbine). In the case of a supercritical-water cooled power reactor, an overall efficiency of 76 % was found; 52 % for the hydrogen production system and 24 % for the turbine. The total energy utilization efficiency for the low-temperature nuclear hydrogen production system above is very high.

This article is organized as follows: Chapter 2 is devoted to describe characteristics of DME as well as its synthesis,
transport and applications. Chapter 3 then gives the calculation procedure and calculated results for hydrogen production fraction in the DME steam reforming process. We also present the calculated total energy utilization efficiency for a nuclear electric power generation plant with an installed hydrogen production system. Additionally, Chapter 4 presents the CO₂ storage and closed CO₂ cycles without CO₂ emission. Finally, we give conclusions in Chapter 5.

II. Characteristics of DME and its synthesis, transportation and applications

In the case of our nuclear hydrogen production system, we use the DME steam reforming process, whose chemical reaction will be described in detail in the next chapter. For the methane (or LPG) steam reforming process, hydrogen is produced industrially at about 773-1173 K from natural gas. Whereas, the reaction temperature for the DME steam reforming process is about 523–575 K and is lower than that for the methane (or LPG) steam reforming process. The low reforming temperature has a merit in that the DME plant does not require materials for a high temperature operation.

The DME reforming process has a further advantage in that it does not involve desulfurization or primary CO transformation. DME is synthesized from (1) natural gas from small or medium-size gas fields, (2) natural gas with a large CO₂ fraction, or (3) coal seam gas as shown in Fig.1. The gas fields containing natural gas of this kind are located in Oceania and Asia. The synthesis of DME from this natural gas is inexpensive compared to the liquefaction of natural gas, because the liquefaction of natural gas at a temperature lower than about 113K needs a larger plant than that required for the DME synthesis. Since DME is liquefied by compression without cooling, it is transported by an LPG ship (or a slightly modified LPG ship). As a result, C.I.F. (cost, insurance and freight) for DME is expected to be lower than that for LNG. This indicates that C.I.F. for DME to Japan will become cheaper than that for LPG. Thus, several industrial groups have announced in the press that transportation of DME to Japan will begin around 2006. In addition, there is a possibility of substituting DME for light oil which produces carcinogenic black smoke when it burns.

As is described in some detail below, the DME synthesis is denoted by a partial oxidation process as a whole and releases heat without emitting CO₂. Additionally, contrary to the usual expectation, we infer that, the hydrogen production cost by DME reforming may be lower than that by LNG reforming, because heat absorbed in DME reforming is smaller than that in LNG reforming.

First, the DME synthesis reaction is presented by

$$2\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}, \quad (1)$$

as a whole, and this reaction is not an endothermic but an exothermic reaction which releases about 160 kJ/mol. The partial oxidation is composed of the following elementary processes denoted as

$$(1/3)\text{CH}_4 + (2/3)\text{O}_2 \rightarrow (1/3)\text{CO}_2 + (2/3)\text{H}_2\text{O}, \quad (2)$$

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2, \quad (3)$$

$$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}, \quad (4)$$

$$(1/3)\text{CO}_2 + \text{H}_2 \rightarrow (1/3)\text{CH}_3\text{OH} + (1/3)\text{H}_2\text{O}, \quad (5)$$

$$(4/3)\text{CH}_3\text{OH} \rightarrow (2/3)\text{CH}_3\text{OCH}_3 + (2/3)\text{H}_2\text{O}. \quad (6)$$

Second, as to the hydrogen production cost, the inference that the hydrogen production cost by DME reforming would be lower than that by LNG reforming is based on the followings.

(1) C.I.F., which is the price of materials shipped to a port in Japan, is expected to be 2.9–3.6 US$/MMBTU for DME and 3.0–5.5 US$/MMBTU for LNG, where MMBTU is million British thermal unit. This indicates that C.I.F. for DME is no more than 1.2 times that for LNG. This is due to the fact that DME is synthesized from inexpensive natural gas or coal seam gas by compact plants, and is liquefied by compression without cooling, unlike LNG.

(2) DME steam reforming does not need processes for desulfurization, CO transformation or materials for high-temperature operation, unlike the LNG case, and the initial cost of DME reforming is expected to be lower than that for LNG reforming.

(3) Absorption heat for DME reforming is about half that in the LNG case, because the LNG reforming process

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \quad (7)$$

requires -165 kJ/(LNG mol), while the corresponding DME reforming process

$$\frac{1}{2}\text{CH}_3\text{OCH}_3 + (3/2)\text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 \quad (8)$$

requires -73.1kJ/(0.5 DME mol). We thus expect DME to be useful for nuclear hydrogen production.
III. Theoretical Analysis of Nuclear hydrogen production by DME reforming

This chapter first gives the calculation method and results for hydrogen production fraction in the DME steam reforming process. The hydrogen production fraction is calculated by the thermodynamic equilibrium analysis. The DME steam reforming chemical reaction is expressed by the following endothermal reactions.

\[ \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2, \quad (9) \]

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2. \quad (10) \]

Although other chemical reaction paths may be considered, the final result is unchanged, since the present analysis treats the thermodynamic equilibrium case. The thermodynamical quantities in the reactor vessel are presented by

\[ K_1 = \frac{P_{\text{CO}_2}^2 P_H^4}{P_{\text{CH}_3\text{OCH}_3} P_{\text{H}_2\text{O}}} = 6.97 \times 10^{35} e^{\frac{2.59 \times 10^3}{T}}, \quad (11) \]

\[ K_2 = \frac{P_{\text{CO}} P_H^2}{P_{\text{CO}_2} P_{\text{H}_2\text{O}}} = 9.49 \times 10^{-3} e^{\frac{4.79 \times 10^3}{T}}, \quad (12) \]

\[ \sum_i m_i x_{m,i} = \sum_i m_i x_{out,i}, \quad (13) \]

\[ P_i = P \frac{x_{out,i}}{\sum_j x_{out,j}}, \quad (14) \]

\[ \Delta h = \sum_i h_{out,i} m_i x_{out,i} - \sum_i h_{in,i} m_i x_{m,i}. \quad (15) \]

The thermodynamical quantities out of the reactor vessel are given by

\[ -\Delta h = w_{out,at} h_{out,at} + w_{out,bw} h_{out,bw} \]

\[ -w_{in,at} h_{in,at} - w_{in,bw} h_{in,bw}. \quad (16) \]

We next investigated the energy utilization efficiency for the hydrogen production and electric power generation when the hydrogen production system is installed. **Figure 4** shows a schematic diagram for a low-temperature nuclear reactor with an installed hydrogen production system. The hydrogen production process is set upstream from a turbine. The calculation was performed for the 573 K steam from the nuclear reactor and 2 MPa DME mixed with the steam. Then, the calculated total energy utilization efficiency according to equilibrium mass and heat balance analysis amounts to about 53%; 30% for the hydrogen production system and 23% for the turbine. This is, to date, the quite high efficiency for low-temperature nuclear reactors. In the case of a fast breeder reactor (FBR) at the medium temperature, the hydrogen production process is set downstream of a turbine. **Figure 5** shows a schematic diagram for FBR with an installed hydrogen production system. The calculation condition that the steam from the nuclear reactor is at 756 K and pressure of the mixture between DME and steam is 2 MPa provides an overall efficiency of 75%; 49% for the hydrogen production system and 26% for the turbine. It is seen that overall efficiency is very high.

Concerning a supercritical-water cooled power reactor (SCPR), **Fig.6** shows a schematic diagram for a reactor with an installed hydrogen production system. In this case, an overall efficiency was found to be 76%; 52% for the hydrogen production system and 24% for the turbine.
IV. CO₂ storage and cycle without CO₂ emission

It is known that PSA (Pressure Swing Adsorption), amine extraction, hydrogen absorption, and membrane (such as polymer membrane) processes are available for CO₂ separation. Concerning the CO₂ storage, underground storage is known to be available. In the storage, CO₂ is confined within hydrates at low temperatures and may precipitate in the form of carbonate minerals. When CO₂ is injected into a coal seam, methane is produced by the CO₂ substitution for methane. In the USA, about 6 % of methane production is gas from coal seam. The economic efficiency of the separation and storage of CO₂ by the nuclear hydrogen production process is higher compared to that by the thermal power generation. This is explained as follows: Total power in the thermal power generation is generated by the combustion with the air composed of nitrogen and oxygen. The CO₂ fraction of the exhaust gas is approximately from 5 to 15 % and the separation of CO₂ needs a process suitable for this low density. If the amine process is adopted for the CO₂ separation, extra heat is necessary to release CO₂ from the amine by raising the temperature up to about 373 K. Then, the turbine efficiency then drops due to the loss of this extra heat. Whereas, the nuclear hydrogen production by the DME steam reforming process operates at about 573 K and does not need the extra heat for the CO₂ absorption/desorption with amine.

The CO₂ emission is reduced by substituting fuel cell vehicles for conventional vehicles, using the hydrogen supply produced by nuclear reactors beyond the 6 % elimination requirement. If further reduction of CO₂ emission is required, the carbon and oxygen atoms composing CO₂ are fixed as the atoms composing DME with hydrogen atoms. To achieve this CO₂ fixing, the emitted CO₂ is transported to the plant, where methane is produced from coal seam by injecting CO₂, by available means of transport such as ships which transport DME from the DME production plant to the hydrogen production plant. DME is synthesized from coal seam.

V. Conclusions

In conclusion, this paper have proposed a novel method of low-temperature nuclear hydrogen production by reforming dimethyl ether (DME) with steam produced by a low-temperature nuclear reactor at about 573 K. The DME steam reforming at low temperatures can use a low-temperature nuclear reactor as a heat. The authors identified conditions that provide high hydrogen production fraction at low pressure and temperatures of about 523-573 K. By setting this low-temperature hydrogen production process at about 573 K upstream from a turbine, it was found theoretically that the total energy utilization efficiency is about 50% and very high. By setting a turbine upstream of the hydrogen production plant, an overall efficiency amounts to 75% for an FBR and 76% for a supercritical-water cooled power reactor (SCPR).
Nomenclature

- $h$: enthalpy
- $hw$: hot water
- $i,j$: CH$_3$OCH$_3$, H$_2$O, H$_2$, CO, CO$_2$
- $K$: equilibrium constant
- $m$: molar mass
- $P$: total pressure (atm)
- $Pi$: partial pressure (atm)
- $st$: steam
- $T$: temperature (K)

$w$: mass flux

$x$: molar flux

References

