Dimethyl ether (DME): a clean fuel/energy for the 21st century and the low carbon society

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Abstract— Dimethyl ether (DME) is the smallest ether, and its chemical formula is CH_3OCH_3. DME usually exists as gas, but it is easy to liquefy by cooling at -25 ^oC at atmospheric pressure and by pressurizing under 0.5 MPa at room temperature. Therefore, DME is easy to handle like liquefied petroleum gas (LPG). DME will be used as a fuel of substitute of LPG. Cetane number of DME is 55-60, so DME will be used as a diesel fuel. DME does not contain poisonous substances, and it burns with no particulate matters (PM), no sulphur oxides (SOx), and less nitrogen oxides (NOx). Therefore, DME is expected as a clean fuel/energy for the 21st century. DME is able to replace light oil and LPG, and its physical properties are similar to those of LPG. It is possible that DME infrastructures will be settled more rapidly than hydrogen, because existing LPG infrastructures can be used for DME. DME is expected as excellent hydrogen/energy carrier and hydrogen storage. It is expected that fuel cell is one of the methods for restraint of global warming and air pollution. For saving our earth and realization of the Low Carbon Society, we should use DME and hydrogen widely.

Keywords— dimethyl ether (DME), clean fuel/energy, hydrogen/energy carrier, low carbon society.

I. Introduction

EMMISION amount of carbon dioxide (CO_2) is rapidly increasing from the Industrial Revolution in 18th century. CO_2 is one of greenhouse gases, causes or leads to the global warming and climate change, and then average temperature of the Earth is rising. The global warming and climate change are occurring. For saving our Earth, this global warming should be stopped. Reducing and utilization of CO_2 are researched and demonstrated. Fuel cell is one of high efficiency energy system, so fuel cell should be used widely. For wide use of fuel cells, huge amount of hydrogen (H_2) will be needed. I recommend low carbon society using hydrogen and dimethyl ether (DME).

II. What is Dimethyl Ether?

DME is the smallest ether. Its molecular formula is CH_3OCH_3, and its molecular weight is 46.07. The boiling point of DME is -25 ^oC, and under ordinary pressure and room temperature DME exists as gas. However, DME is easy to liquefy by being pressurized to 0.53 MPa at 20 ^oC and by being cooled to less than -25 ^oC under 0.1 MPa [1, 2]. Because the physical properties of DME resemble those of propane and butane which are the main ingredient of liquefied petroleum gas (LPG), storage and handling of DME can apply the technology for LPG, and the existing infrastructure of LPG can be used for DME by improving the sealing materials. In addition, DME is a clean fuel that does not contain sulphur or any nitrogen compound, and DME does not corrode metal. DME decomposes to CO_2 and H_2O by a photochemical reaction within 3-30 h in the atmosphere, so the greenhouse effect and the ozone depletion effect are not accepted. DME is a dim, sweet-smelling gas that is colourless at room temperature and atmospheric pressure. Its gas density is heavier than air and DME has high solubility for some chemical products, and is chemically and thermally stable. DME has moderate vapour pressure and very low toxicity in the human body. Therefore, DME is now widely used as a spray agent for aerosol, and a propellant, like LPG.

DME has a molar heat capacity under standard pressure and temperature (C_p; 298 K) of 60.71 J mol^{-1} K^{-1}. This value is higher (by ~65%) than that of methane (natural gas), and is higher by approximately 40% than that of methanol. Compared with LPG, the value of DME is approximately 65% less than that of LPG due to the difference in the chemical structure. However, DME can be stored as a material with approximately 90% of the LPG heat capacity in a tank of the same size because the liquid density of DME is higher than that of LPG. Moreover, DME is more excellent as a clean fuel for diesel engine compared with the light oil currently used as a diesel fuel. The cetane number of DME for self-ignition is 55-60 and this value is the same level as light oil. DME burns without particulate matters (PM) such as dark smoke etc., because oxygen is contained and there is no C-C bonding in DME (CH_3OCH_3) unit. DME also burns with no generation of sulphur oxides (SOx) because it had no sulphur content. In addition, the generation of nitrogen oxides (NOx) can be decreased by 20-30%. Therefore, there is great hope for DME as a diesel engine substitution fuel. In Japan, China, Sweden, Korea, and USA, some diesel engine trucks and buses have been being demonstrated and /or used on public roads. Moreover, it is a useful fuel for household, heater, turbine, and power-generation plant gas for these LPG infrastructures. If DME is used for these fuels rather than coal, heavy oil, and LPG; the emission of PM, NOx, SOx, and CO_2 will decrease. In addition, DME is strongly favoured as a hydrogen carrier and

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hydrogen source of fuel cells. From the recent research on DME steam-reforming catalysts, hydrogen will be produced effectively from DME. It is speculated that the DME steam-reforming hydrogen generator can be a smaller hydrogen supply system compared with the high-pressure hydrogen gas cylinder (70 MPa) and hydrogen storage alloy (3 wt.%), and DME is the most promising material for hydrogen storage and as a hydrogen carrier [3-5]. Therefore, DME is so-called “clean fuel/energy for 21st century” [2, 6]. DME is mainly produced from methanol, and methanol is produced from syngas (synthesis gas; mixed gas with hydrogen and carbon monoxide). The syngas is produced from natural gas, coal, coal bed methane, biomass, and so on. Therefore, DME is a multi-use and multi-source fuel.

III. DME AS A HYDROGEN/ENERGY CARRIER AND STORAGE

DME is mainly produced by dehydration of methanol and is a byproduct of the methanol manufacturing process. However, DME and new technologies for DME production have recently drawn attention as contributors to creating a stable energy supply and demand in the future. They also have environmental benefits because DME is produced through syngas from multiple sources. There are two methods of industrialized and demonstrated new technologies for DME production: indirect DME synthesis (a two-step process) and direct DME synthesis (a one-step process). For the indirect-synthesis method, methanol is produced from syngas and the produced methanol is dehydrated to DME; these two processes are carried out in different reactors. In the direct-synthesis method, DME is produced from syngas directly in a reactor.

A. Indirect DME synthesis method (a two-step process)

Methanol is produced by a methanol synthesis process from syngas (Equation 1).

$$CO + 2H_2 \rightarrow CH_3OH \qquad (1)$$

Purified methanol manufactured by the methanol-synthesis process or raw methanol separated from syngas in the methanol-synthesis process are converted into DME by the dehydration process (in this case, etherification) (Equation 2).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (2)$$

This method uses an existing methanol-synthesis and dehydration process, and so there is less need for the development of technologies and catalysts. For methanol synthesis, existing methanol-synthesis catalysts are used and the catalysts are usually copper based. For methanol dehydration, solid catalysts such as γ-alumina, zeolite and sulfuric acid are used. Therefore, costs for development are also reduced. The rationalized industrial plant can be installed promptly. However, the system will be complicated because the products are a mixture of DME, methanol and water, and thus distillation, purification and recycling processes will be needed. The price of DME depends on the price of methanol, with the DME price usually approximately twice that of methanol. This is a big problem for this method. There are some disadvantages, as discussed previously, but all industrial DME plants in the world use this indirect DME-synthesis method.

B. Direct DME-synthesis method (a one-step process)

The merit of the direct synthesis method is that the manufacturing process is economical because the methanol synthesis and dehydration processes are performed in one reactor. The equilibrium conversion of syngas is much higher compared with the conversion of the methanol synthesis, and it is possible to reduce the unreacted gas ratio so that it is very low. The reaction equation of the direct synthesis method is shown in Equation 3; copper-based catalysts are used for this method as they are very effective in the water–gas shift reaction. Therefore, this method is more suitable to use with CO-rich gas than methanol synthesis and indirect DME synthesis.

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad (3)$$

This method is known as the one-step process, but actually consists of three reaction steps: methanol synthesis (Equation 4), methanol dehydration (Equation 5) and the water–gas shift reaction (Equation 6). For methanol synthesis, copper-based catalysts are usually used. The copper-based catalysts work for the water–gas shift reaction, which occurs by H_2O produced from the methanol dehydration and CO in the same reactor.

$$CO + 2H_2 \rightarrow CH_3OH \qquad (4)$$
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (5)$$
$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (6)$$

From this reaction mechanism, a mixture of the methanol-synthesis catalysts, methanol-dehydration catalysts and water–gas shift reaction catalysts is used. Slurry reactors and fixed-bed reactors have been developed for this process by some companies [7,8]. In Japan, a consortium under the leadership of JFE Holdings, Inc. demonstrated a 100-tons/day plant from 2002 to 2006 as a national project. This project achieved the target values and was finished successfully. The reaction temperature was 260 °C, the reaction pressure was 5.0 MPa and the gas velocity was 40 cm/s. The total conversion was 96%, the DME production rate was 109 tons/day and the DME purity was 99.8%. The reactor was a slurry reactor, because this reaction produces much heat and the slurry dispersed the reaction heat [9-13]. In Korea, Korea Gas Corp. (KOGAS) demonstrated a 10-tons/day direct DME-synthesis plant. The reaction temperature was 260 °C, the reaction pressure was 6.0 MPa and the space velocity of reaction gas was 2000 h^{-1}. The reactor was a fixed-bed reactor and was cooled by 230 °C hot water. KOGAS is targeting commercial 3000-tons/year plants [14-16].

C. Steam reforming of DME

Hydrogen can be produced by steam reforming of DME. Hydrogen production by steam reforming of DME (SRDME) consists of two steps: the first is DME hydrolysis, and the second is steam reforming of methanol (SRM). The chemical equation of SRDME (Equation 7) is separated for that of DME hydrolysis (Equation 8) and that of SRM (Equation 9), as follows:

$$CH_3OCH_3 + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad \text{(steam reforming of DME)}, \qquad (7)$$

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH \quad \text{(hydrolysis of DME)}, \qquad (8)$$

$$2CH_3OH + 2H_2O \rightarrow 6H_2 + 2CO_2 \quad \text{(steam reforming of methanol)}. \qquad (9)$$

From these reaction mechanisms, mixture of DME hydrolysis catalyst and methanol steam reforming are used for DME steam reforming and the hydrogen production. Almost all researchers [17-33] have reported about mixed catalysts, but we focused on single-use-type catalysts prepared by the sol-gel method in terms of catalyst life and for ease of industrial processing that eliminate the mechanical mixing procedure. The copper-based alumina catalysts prepared by the sol-gel method in the single use produce more hydrogen than mixed catalysts by commercial catalysts of DME hydrolysis and SRM [34-36]. These copper alumina catalysts prepared by sol-gel methods are also more effective in direct DME synthesis from CO and/or CO_2 than mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts [37-39].

D. Comparison on steam reforming of other fuels

Figure 1 shows temperature dependence of equilibrium conversion of DME, methanol, light oil, gasoline, propane, and natural gas (methane) [39]. Natural gas (NG), propane, gasoline, and light oil are difficult for hydrogen production and reforming, and high reaction temperature and heat energy are needed for hydrogen production by their reforming reaction. On the other hand, methanol and DME are easy to reform for hydrogen production.

In practical case of methane steam reforming for hydrogen production, reaction temperature is usually 800-950 ^{o}C. Their chemical reaction equations and heat energy show in the following equations:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 - 167\ \text{kJ mol}^{-1} \quad (41.8\ \text{kJ}\ (H_2\ \text{mol})^{-1}) \qquad (10)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 - 206\ \text{kJ mol}^{-1} \quad (\text{at } 800 - 950\ ^{o}\text{C}) \qquad (11)$$

$$CO + H_2O \rightarrow CO_2 + H_2 + 39\ \text{kJ mol}^{-1} \quad (\text{at } 180 - 450\ ^{o}\text{C}) \qquad (12)$$

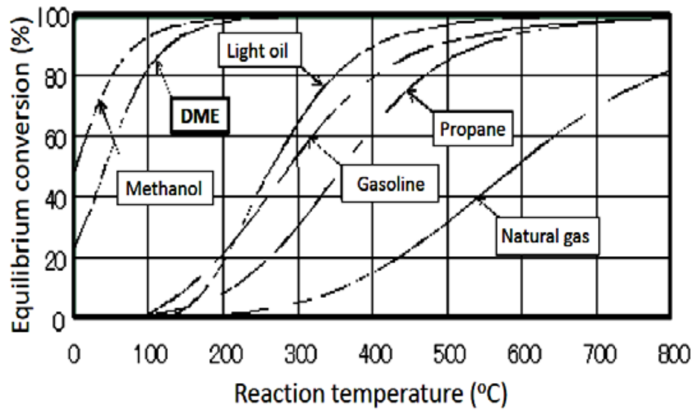

Fig. 1. Temperature dependence of equilibrium conversion of various fuels for hydrogen production by their reforming reaction [40]

CH_4 is steam reformed to H_2 and CO at 800 – 950 ^{o}C, and water gas shift reaction is occurred with produced CO and H_2O. Methane steam reforming is is an endothermic reaction, and totally 167 kJ mol^{-1} is needed for the reaction. For production of 1-mol H_2, 41.8 kJ is needed.

On the other hand, DME steam reforming is carried out at 250 – 400 ^{o}C, and 1- mol H_2 can be produced by 24.3 kJ.

$$CH_3OCH_3 + 3H_2O \rightarrow 2CO_2 + 6H_2 - 146\ \text{kJ mol}^{-1} \quad (24.3\ \text{kJ}\ (H_2\ \text{mol})^{-1})\ (\text{at } 250 - 400\ ^{o}\text{C}) \qquad (13)$$

Therefore, hydrogen can be produced easier from DME than from methane and/or NG, and H_2 production from DME is more eco-friendly and better for the Earth than from methane or NG.

DME has a large weight fraction of hydrogen. Hydrogen constitutes 13.0% of the mass of DME. DME is easy to liquefy by being pressurized to 0.53 MPa at 20 ^{o}C and by being cooled to less than -25 ^{o}C under 0.1 MPa. On the other hand, boiling point of hydrogen and NG are -253 ^{o}C and -162 ^{o}C, respectively (*Cf.* Table 1 [1]). They are very difficult for handling. Therefore, DME is the most promising material for hydrogen storage and as a hydrogen carrier [3-5].

IV. LOW CARBON SOCIETY USING HYDROGEN AND DME

DME synthesis from hydrogen and CO can be thought as "hydrogen storage" process, and DME steam reforming can be thought as "hydrogen production" process. Hydrogen handling such as storage and transportation can be managed by using DME. Figure 2 shows a conceptual figure of DME-hydrogen chain for low-carbon society. H_2 and CO are produced from biomass, coal, NG, and so on. On the other hand, H_2 is obtained from water electrolysis by using sustainable energies such as solar, wind powers, and so on. CO_2 is also utilized for DME synthesis in order to reduce amount of CO_2 in air for restraint of global warming and air pollution.

$$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \qquad (14)$$

Table 1 Fundamental properties comparison between dimethyl ether (DME) and other fuels [1]

	Unit	DME	Propane	Kerosene	Gasoline	Methanol	Ethanol	Hydrogen	CNG (Methane)
Liquid density	Kg/m^3	667	500.5	831	750	795	789	—	—
Gas specific gravity (viaAir, Air=1)		1.59	1.52	—	—	—	—	0.07	0.56
Cetane number		55 - 60	—	40 - 55	—	3	8	—	—
Research octane number		—	112.1	—	98	106	107	—	120
Theoretical oxygen ratio	kg/kg	9.0	15.88	14.6	14.7	6.46	9	34.2	16.86
Boiling point	°C	-25	-42	180/370	30/190	65	78	-253	-162
Low heating value	MJ/kg	28.8	46.35	42.7	43.2	19.8	26.4	120	49
Explosion limit	%	3.4 - 17	2.1 - 9.4	0.6 - 6.5	1.4 - 7.6	5.5 - 36	3.3 - 19	4.1 - 74	5.0 - 15
Vapor pressure	kPa (@293K)	530	830	—	—	37	21	—	—
Molecular weight	/mo1	46.07	44.09	170	98	32.04	46.07	2.01	17
Flash point	°C	235	470	250	—	450	420	—	650
Heat of vaporization	kJ/kg	467.13	372.00	300	420	1110	845	460	510

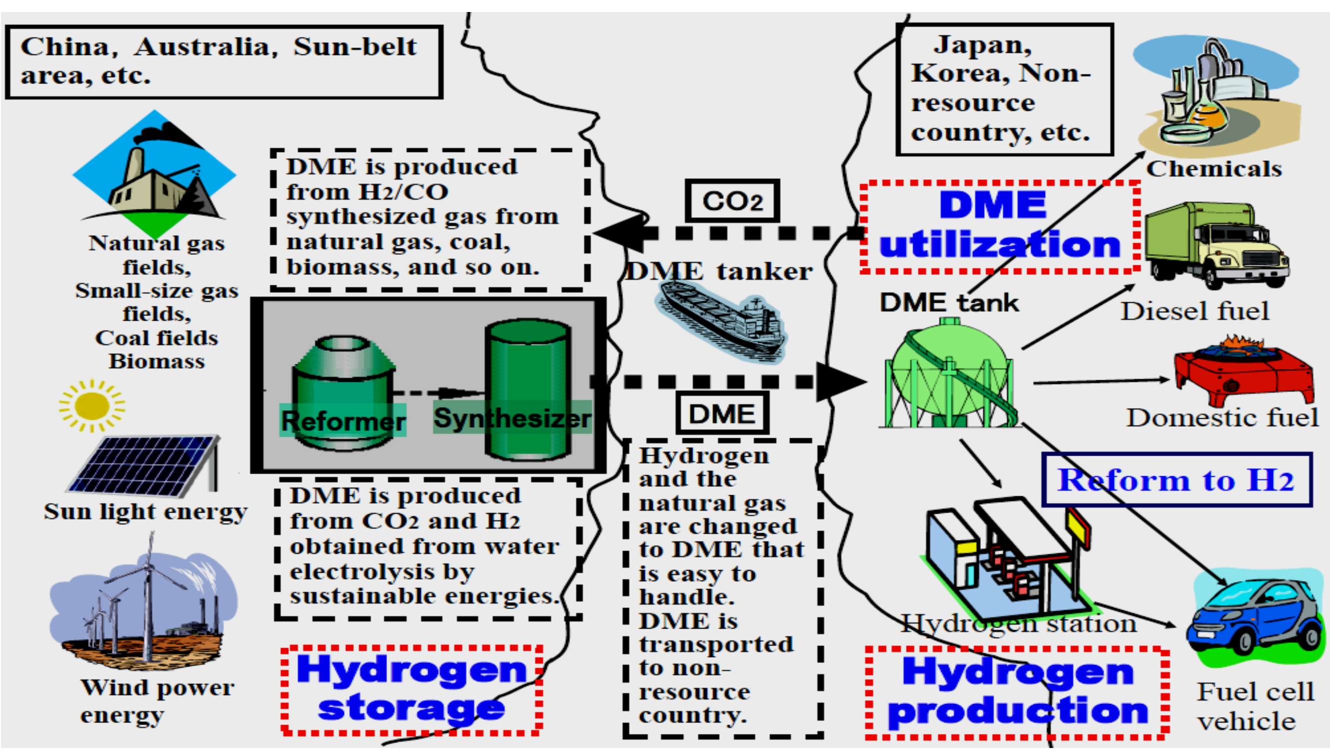

Fig. 2. Conceptual figure of DME-hydrogen chain for low carbon society [41].

Produced DME in China, Australia, sun-belt areas, and so on is transformed to non-recourses countries such as Japan, Korea, and other countries by DME tankers. DME is used for fuel, chemicals, raw-materials of chemicals, and so on. The other DME is steam-reformed to hydrogen, and produced hydrogen is used for fuel cells. Empty tankers transform CO_2 produced at power plants, factories, DME reformers, and so on to sun-belt areas, Australia, China, and other countries for utilizing of DME synthesis and carbon dioxide capture and storage (CCS) into underground deeper than 1,000 m.

We think that this low carbon society using DME, H_2, and CO_2 will solve the global warming, air pollution, and save our Earth.

V. Conclusion

DME is a clean fuel/energy, and a hydrogen/energy carrier and storage. DME should be widely used for restraint of the global warming and air pollution. We must introduce the low carbon society using DME, H_2, and CO_2 as fast as possible for saving our Earth.

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