

Chemical Recuperation of Low-Grade Exhaust Heat by Steam Reforming of Dimethyl Ether

*Mr. Ken Tsuzuki, Graduate School of Engineering, Nagoya University, Nagoya, Aichi, Japan,
Dr. Noriyuki Kobayashi, EcoTopia Science Institute, Nagoya University, Nagoya, Aichi, Japan,
Dr. Tsuguhiko Nakagawa, JFE R&D Corporation, Kawasaki, Kanagawa, Japan,
Dr. Hitoshi Saima, JFE R&D Corporation, Kawasaki, Kanagawa, Japan,*

Abstract

For the new process of effective utilization of energy, chemical recuperation of low-grade exhaust heat by steam reforming of dimethyl ether (DME) was proposed. Steam reforming of DME is an endothermic reaction as; $\text{DME} + 3\text{H}_2\text{O} + 122[\text{kJ/mol}] \rightarrow 6\text{H}_2 + 2\text{CO}_2$. If this reaction could be proceeded by exhaust heat below 573 [K], those exhaust heat which is wasted to ambient would be recuperated as the fuel with increasing exergy. In this study, a fixed bed type reactor was adopted experimentally. Catalytic activity for steam reforming of DME was estimated in the atmospheric pressure, the S/C=1.55 and reaction temperature of 523 [K] to 573 [K] as a practical condition. As a result, highly conversion of DME was confirmed around 523 [K].

Introduction

Energy consumption that would cause several fatal environmental problems all over the world, have been growing. Problems such as soaring of fuel price have been actualized. Under those circumstances, the securement of stability supply for energy, the prevention of the global warming, or the establishment of the new energy supply system which have aspects of high energy efficiency and furthermore, environmental friendly is required.

The cascading system of energy use has been developed after oil crisis, and the highly effective use for energy has been promoted. A lot of attempts to use of exhaust heat have been executed through the process of a variety of economic activities. For instance, the exhaust heat has been used as the steam for the heating of the fuel in all the chemical plants. These efforts to recovering exhaust heat are directly concerned with saving primary energy supply, and excellent solution for energy problems such as the global warming and so on.

However many trial has been done, the case that energy could not be used effectively has come out. That is because three disproportions. Firstly, the heat source site and the demand ground are in long distance geographically. Secondly, the mismatch in time between the demand and supply of the heat exists. Thirdly, the exergic quality of the exhaust heat is not suitable to the requirement to the demand. Besides, with sensible heat, being transported, stored, or transformed to electric energy is difficult. According to a quantitative investigation of the exhaust heat, the amount of the exhaust heat discharged in the atmosphere as unused is about three times of energy consumption. Especially, utilization of low-grade exhaust heat of below 573 [K] is difficult; energy is wasted to the ambient. If the exhaust heat energy could be recuperated to a fuel that it is possible to be transported and stored, those problems would be dissolved.

In this study, the process was proposed that chemically recuperates the exhaust heat to a fuel by reforming of dimethyl ether, DME. The empirical examination in regard to the feasibility of

that process was discussed. Nowadays, DME have attracted much attention as a petroleum substitute fuel [1], which is synthesized from even low-grade gas fields or biomass [2]-[3], and also as one of hydrogen resources having high energy density. Especially, reforming of DME is performed in relatively low temperature between 523 [K] and 673 [K] and the reforming of DME is an endothermic reaction as follows.

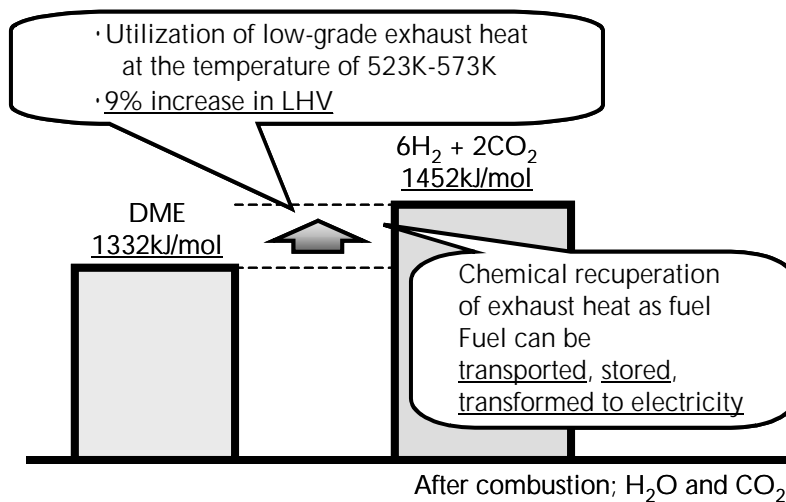
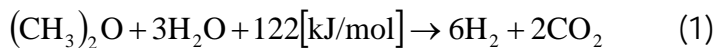
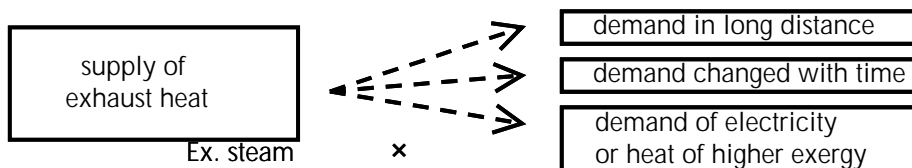


Fig.1 Comparison for LHV

Existing process of exhaust heat utilization



Chemical recuperation of exhaust heat by DME steam reforming

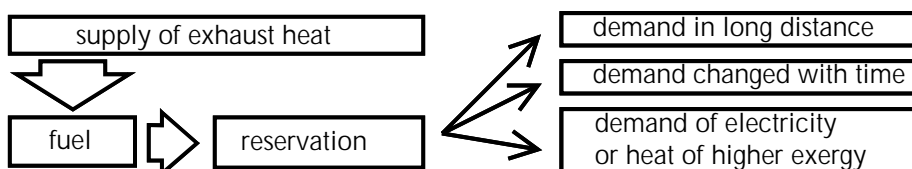


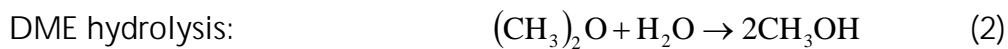
Fig.2 Expected merits of the proposed process of this study

The lower heating value of effluents is 1453 [kJ/mol] that is 9% higher than that of reactant DME (1332 [kJ/mol]). If the exhaust heat energy would be used for the reforming process, the exhaust heat energy could be recuperated as hydrogen, fuels of high quality. The image and the merits of this process are shown in Fig.1 and Fig.2 respectively.

It is also possible to recuperate exhaust heat to hydrogen by steam reforming of alcohols such as methanol [4]-[7]. However, DME have other competent advantages. DME has already penetrated the commercial sector as aerosol propellants with typical uses in bronchodilators, shaving cream, perfume and spray paint, etc. DME can be used as diesel substitute. When applying to diesel cycle, DME decreases NO_x, SO_x, or particulate matter

emissions [8]. The storage and handling of DME is similar to those of liquefied petroleum gases (LPG); e.g., butane and propane. Therefore the infrastructure of LPG fuels can be readily used for the distribution of DME. The existing natural gas infrastructure can be used to distribute DME. Besides, DME is relatively inert, noncorrosive, and noncarcinogenic, thus showing promise for reducing pollutants and providing cleaner air. Consequently, DME is a promising alternative fuel for variety energy carrier. Therefore, a lot of investigations, which is related to DME reforming or synthesis, combustion, has been in progress.

For the steam reforming of DME, some studies has been investigated from the view point of the development of catalyst, and advanced catalyst with high conversion rate in lower temperature of 600 [K] have been developed. Steam reforming of DME is composed of two consecutive reactions [10]-[11]. The first step reaction is the hydration of DME to form methanol over solid acid catalysts: (2). And the second step reaction is the steam reforming of methanol: (3)



The overall reaction is expressed by equation (1). The equilibrium conversion of hydration of DME is low (about 22.7% at 573 [K], steam to carbon ratio S/C=1.5). However, when methanol formed in the first step reaction is rapidly converted into H₂ and CO₂ by methanol steam reforming catalysts, high DME conversion is expected. From many research, it have been considered that catalysts, which have a lot of Lewis acid sites, accelerate the DME hydrolysis. Alumina, zeolite, or silica that have many active sites has been applied [13]-[21]. With steam reforming methanol, Cu based catalysts have been used typically. Thus mixed catalysts of those are much discussed in terms of active species or compositions.

The development of the reformer, which can obtain highly conversion of DME at around the temperature of 773 [K], has been in progress now to apply for the fuel cell [11] or the chemically recuperated gas turbine system [12]. Compared with those investigations, this study has some different aspect. In terms of energy recuperation, the system, which can collect much heat as much as possible at low temperature, is better. In case the temperature of exhaust heat is low or the quantity of exhaust heat is small, the improvement design of reactor, which can obtain sufficient conversion ratio, must be necessary. The feasibility study and development of the system, which it can correspond to those requests in utilization, are necessary. The required feature of device for energy recuperation process is simple structure, cheap, and easy maintenance. For reformer, fixed bed type, fluidized bed type or reaction and heat transfer monolithic type is considered. When use with practical process is assumed, the fixed bed type, whose maintenance is easy with simple structure, has big advantage. In regard to the optimization, quantization of rate equation becomes necessary. Some investigations concerning the individual catalyst for the purpose of reforming in low temperature with high reaction ratio have been done, however the kinetics of reaction has not been investigated yet. Although the reactor of fixed bed type have been used for the measurement of the catalyst reaction, only the measurements have been done with the identical W/F as a conditional setting of experiment, or under the dilution conditions with inert gas to measure the instinctive character of each catalyst.

Experimental

In this study, the reactor of fixed bed type was adopted experimentally. Catalytic activity for steam reforming of DME was estimated in the atmospheric pressure, the S/C=1.55 and reaction temperature of 523 [K] to 573 [K] as the practical conditions for the purpose of chemical recuperation of low-grade heat. Furthermore, by changing the W/F [g-cat h/mol], in other words, changing catalyst bed thickness, fundamental experiment was investigated in regard to the design of the fixed bed reactor.

Catalytic activity was estimated using a fixed-bed flow quartz reactor with the internal diameter of 10 mm at 523 K to 573 K in the temperature. The catalyst of 1 mg or 4 mg was placed inside the reactor on silica wool. The catalysts were contributed by JFE Co. Major component of that catalyst are copper and alumina. The catalysts heated under a H₂ flow of 20 ml/min. for 120 min. at 573 K prior to the measurements. The feed mixture with steam/DME = 3.1 was allowed to pass through the reactor at a flow rate of 82 ml/min. (W/F = 10 to 80 g-cat h/mol) at the maximum. The flow rate of all gas reactants was maintained by the mass flow controllers (KOFLOC 3600 and 5100). Liquid water maintained by syringe pump was vaporized and mixed with other gas reactant through the evaporator. The temperature of the evaporator or preheated section of equipments is 413 K. Each catalyst can be pre-treated and heated for the same treatment time with this experimental setup. The effluents were analyzed by two sets of gas chromatographs (yanaco G-2700) equipped with the thermal conductivity detectors and capillary columns with He and N₂ carrier. H₂, CO₂, CO, DME, and traces of CH₄ were the only products detected under the present experimental conditions. Conversion of DME and the selectivity of hydrogen were calculated from the quantity and composition of effluents. The schematic diagram of equipment is shown in Fig.3. The fraction of methanol was calculated from hydrogen selectivity.

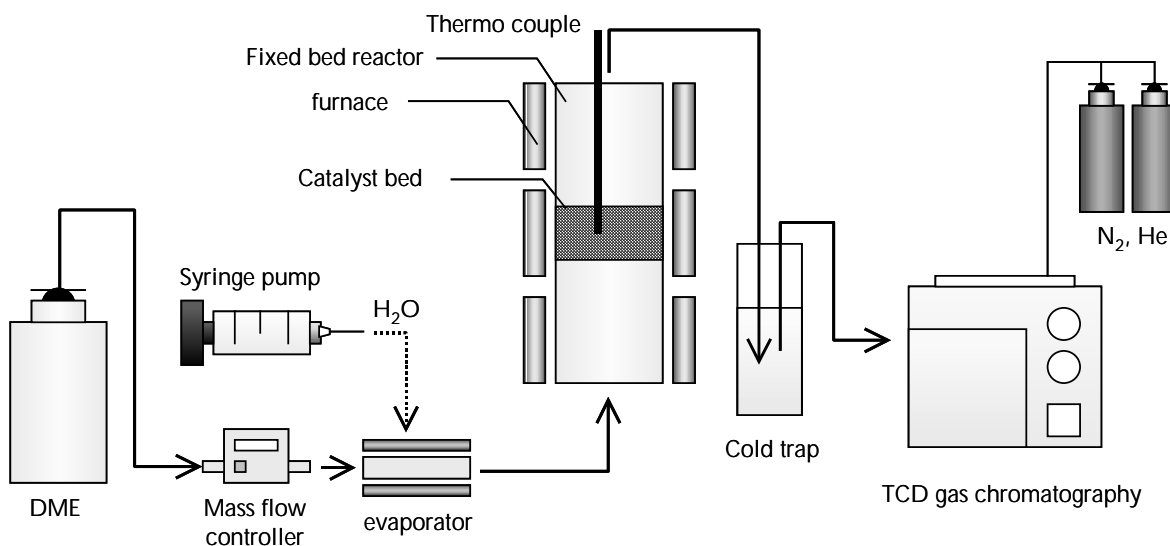


Fig.3 Schematic diagram of experimental equipments

Results and discussions

From the results of experiments at the temperature of 573 K shown in Fig.4, increase in conversion ratio of DME and selectivity ratio of hydrogen with increase of W/F was confirmed. Approximately 100% conversion ratio of DME and selectivity ratio of hydrogen were achieved at W/F of 40 g-cat h/mol. The composition of effluent gas was consisted of mixture of 74.6% hydrogen, 19.8% carbon dioxide, and 5.6% carbon monoxide, lower than 1% DME, methanol and methane as shown in Fig.4. In lower W/F range, formation of methanol was confirmed. As mentioned above, the steam reforming of DME is composed of two consecutive reactions. The first step is the hydration of DME to form methanol over solid acid catalysts such as alumina: equation (2), and is followed by the steam reforming of methanol: equation (3). On the other hand, in higher W/F range, formation of CO or CH₄ was confirmed. The reverse water gas shift reaction; $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$, and the methanation reaction; $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$, were seemed to occur simultaneously.

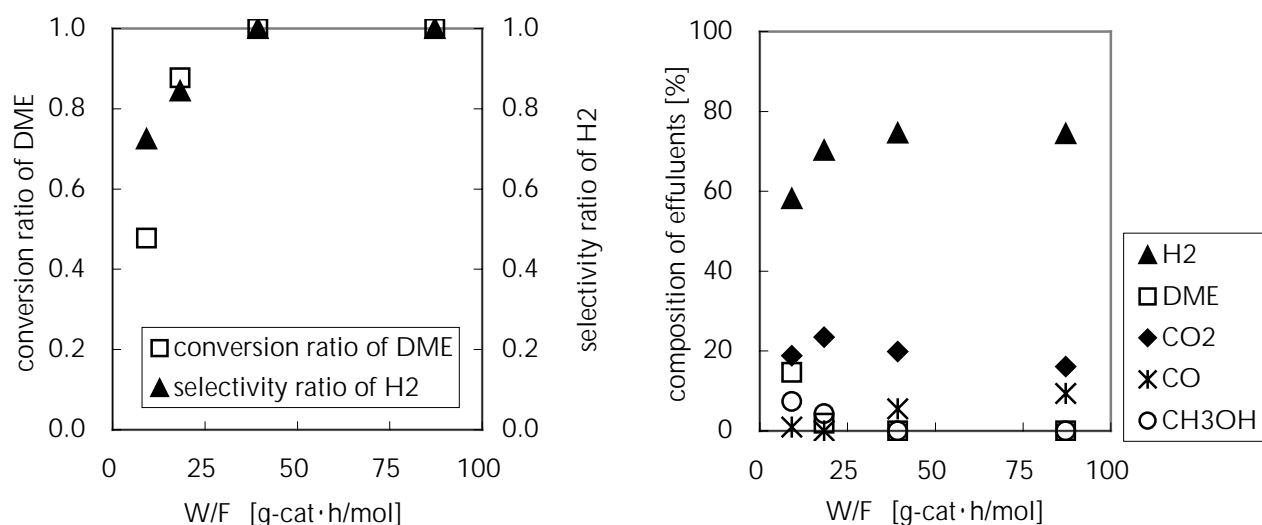


Fig.4 Steam reforming of DME at the temperature of 573K

For the purpose of observation of catalytic activity at lower temperature, steam reforming of DME also examined at 523 K shown in Fig.5. From results of the experiments, high conversion ratio of DME and selectivity of hydrogen was confirmed. The composition of the effluent gas consisted of the mixture of 74.3% hydrogen, 22.7% carbon dioxide, 2% methanol, 1% DME. Carbon oxide and methane was lower than 1% as shown in Fig.5. The lower heating vale was increased by 8.9% compared to the reactant DME.

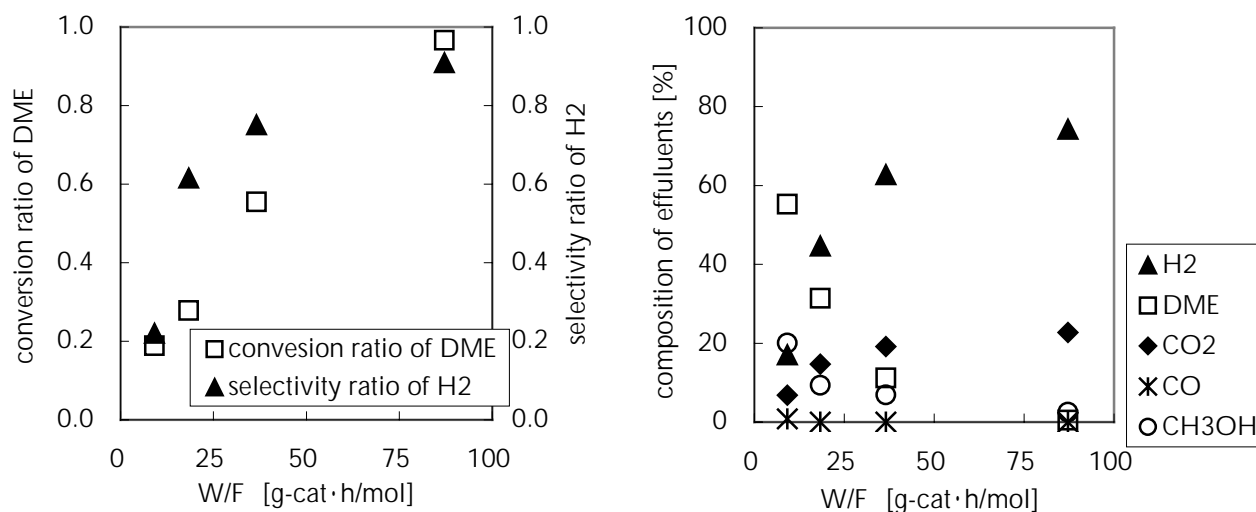


Fig.5 Steam reforming of DME at the temperature of 523K

Conclusions

Highly conversion of DME with steam was confirmed around 523 K with the lab-scale reactor in the practical condition. Approximately 100% conversion ratio of DME as well as 100% selectivity of H₂ was achieved at W/F of 40 g-cat h/mol at 573K.

The process of chemical recuperation of low-grade exhaust heat is promised to be applied enough at the temperature of 523K to 573K.

Reference

1. Troy A. Semelsberger, Rodney L. Borup, Howard L. Greene, *Journal of Power Sources* 156 (2006) 497–511
2. K.L. Ng, D. Chadwick, B.A. Toseland, *Chemical Engineering Science* 54 (1999) 3587-3592
3. Wen-Zhi Lu, Li-Hua Teng, Wen-De Xiao, *Chemical Engineering Science* 59 (2004) 5455 – 5464
4. Yongtaek Choia, Harvey G. Stengerb, *Journal of Power Sources* 142 (2005) 81–91
5. A. Mastalir, B. Frankb, A. Szizybalski, H. Soerijanto, A. Deshpande, M. Niederberger, *Journal of Catalysis* 230 (2005) 464–475
6. Liwei Pan, Shudong Wang, *Chemical Engineering Journal* 108 (2005) 51–58
7. Liwei Pan, Shudong Wang, *International Journal of Hydrogen Energy* 30 (2005) 973 – 979
8. Hiroyuki Yamada, Kotaro Suzaki, Hideki Sakanashi, Namil Choi, Atsumu Tezaki, *Combustion and Flame* 140 (2005) 24–33
9. Troy A. Semelsberger, Rodney L. Borup, *Journal of Power Sources* 152 (2005) 87–96

10. Troy A. Semelsberger, Kevin C. Ott, Rodney L. Borup, Howard L. Greene, *Applied Catalysis B: Environmental* 61 (2005) 281–287
11. Jung-Han Yoo, Hoo-Gon Choi, Chan-Hwa Chunga, Sung Min Choa, *Journal of Power Sources* Available online 26 July 2006
12. Daniele Cocco, Vittorio Tola, Giorgio Cau, *Energy* 31 (2006) 1446–1458
13. Yohei Tanaka, Ryuji Kikuchi, Tatsuya Takeguchi, Koichi Eguchi, *Applied Catalysis B: Environmental* 57 (2005) 211–222
14. Troy A. Semelsberger, Kevin C. Ott, Rodney L. Borup, Howard L. Greene, *Applied Catalysis A: General* 309 (2006) 210–223
15. Thomas Mathewa, Yusuke Yamada, Atsushi Ueda, Hiroshi Shioyama, Tetsuhiko Kobayashi, Chinnakonda S. Gopinath, *Applied Catalysis A: General* 300 (2006) 58–66
16. Thomas Mathew, Yusuke Yamada, Atsushi Ueda, Hiroshi Shioyama, Tetsuhiko Kobayashi, *Applied Catalysis A: General* 286 (2005) 11–22
17. Toshiya Nishiguchi, Kengo Oka, Tomoaki Matsumoto, Hiroyoshi Kanai, Kazunori Utani, Seiichiro Imamura, *Applied Catalysis A: General* 301 (2006) 66–74
18. V.V. Galvita, G.L. Semin, V.D. Belyaev, T.M. Yurieva, V.A. Sobyenin, *Applied Catalysis A: General* 216 (2001) 85–90
19. Kaoru Takeishi, Hiromitsu Suzuki, *Applied Catalysis A: General* 260 (2004) 111–117
20. Tomoaki Matsumotoa, Toshiya Nishiguchia, Hiroyoshi Kanaia, Kazunori Utani, Yasuyuki Matsumura, Seiichiro Imamura, *Applied Catalysis A: General* 276 (2004) 267–273
21. Yusuke Yamada, Thomas Mathew, Atsushi Ueda, Hiroshi Shioyama, Tetsuhiko Kobayashi, *Applied Surface Science* 252 (2006) 2593–2597