

Thermodynamic equilibrium calculations of dimethyl ether steam reforming and dimethyl ether hydrolysis[☆]

Troy A. Semelsberger*, Rodney L. Borup

Materials Science and Technology Division, Los Alamos National Laboratory, P.O. Box 1663, Mail Stop J579, Los Alamos, NM 87545, USA

Received 30 November 2004; received in revised form 12 January 2005; accepted 12 January 2005

Available online 28 March 2005

Abstract

The production of a hydrogen-rich fuel-cell feed by dimethyl ether (DME) steam reforming was investigated using calculations of thermodynamic equilibrium as a function of steam-to-carbon ratio (0.00–4.00), temperature (100–600 °C), pressure (1–5 atm), and product species. Species considered were acetone, acetylene, carbon dioxide, carbon monoxide, dimethyl ether, ethane, ethanol, ethylene, formaldehyde, formic acid, hydrogen, isopropanol, methane, methanol, methyl-ethyl ether, *n*-propanol and water.

Thermodynamic equilibrium calculations of DME steam reforming indicate complete conversion of dimethyl ether to hydrogen, carbon monoxide and carbon dioxide at temperatures greater than 200 °C and steam-to-carbon ratios greater than 1.25 at atmospheric pressure ($P = 1$ atm). Increasing the operating pressure shifts the equilibrium toward the reactants; increasing the pressure from 1 to 5 atm decreases the conversion of dimethyl ether from 99.5 to 76.2%. The trend of thermodynamically stable products in decreasing mole fraction is methane, ethane, isopropyl alcohol, acetone, *n*-propanol, ethylene, ethanol, methyl-ethyl ether and methanol–formaldehyde, formic acid, and acetylene were not observed. Based on the equilibrium calculations, the optimal processing conditions for dimethyl ether steam reforming occur at a steam-to-carbon ratio of 1.50, a pressure of 1 atm, and a temperature of 200 °C. These thermodynamic equilibrium calculations show dimethyl ether processed with steam will produce hydrogen-rich fuel-cell feeds—with hydrogen concentrations exceeding 70%.

The conversion of dimethyl ether via hydrolysis (considering methanol as the only product) is limited by thermodynamic equilibrium. Equilibrium conversion increases with temperature and steam-to-carbon ratio. A maximum dimethyl ether conversion of 62% is achieved at a steam-to-carbon ratio of 5.00 and a processing temperature of 600 °C.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Dimethyl ether; Steam reforming; Fuel cells; Methanol; Hydrolysis; Hydrogen

1. Introduction

Alternative and renewable energy technologies are being sought throughout the world to reduce pollutant emissions and increase the efficiency of energy use. Fuel cell technology is one approach that is being researched to improve energy efficiency. Oil is the main source of energy in the United States for transportation; however, with the advent of more efficient methods of producing power, such as fuel cells, the depen-

dency on foreign oil can be relaxed, though not removed. A means of removing the dependency on foreign oil is to use fuels derived from renewable sources such as Fischer–Tropsch fuels or fuels such as methane, biomass and coal. For this reason, methanol, ethanol, biodiesel and biogasoline are researched.

Dimethyl ether (DME) is an alternative fuel that has not attracted much attention as a hydrogen carrier for fuel cells, although it has good potential because it reforms at low temperatures [1–11]. Turn-over-frequencies as high as 4.2×10^{-6} mol of dimethyl ether per gram of catalyst per second ($T = 275$ °C, $\tau = 1.0$ s) have been observed with the complete conversion of dimethyl ether to hydrogen, carbon monoxide and carbon dioxide [9,11]. The production of

[☆] This paper was presented at the 2004 Fuel Cell Seminar, San Antonio, TX, USA.

* Corresponding author. Tel.: +1 505 665 4766; fax: +1 505 665 9507.

E-mail address: troy@lanl.gov (T.A. Semelsberger).

dimethyl ether occurs over zeolite-based catalysts with syngas as the raw material, thus the feedstock can be traditional hydrocarbons or renewable sources [12–23]. Unlike many fuels considered for the production of hydrogen-rich fuel-cell feeds, dimethyl ether is nontoxic, noncarcinogenic, nonteratogenic and nonmutagenic. Dimethyl ether has already penetrated the commercial sector as aerosol propellants (e.g., DuPont™ Dymel A®) with typical uses in bronchodilators, shaving cream, perfume and spray paint.

Dimethyl ether has been used as a refrigerant and diesel substitute and additive [1,24–33]. Used as either a diesel substitute or additive, dimethyl ether decreased NO_x, SO_x, and particulate matter emissions [26,34–36]. Because dimethyl ether burns cleanly, it is being considered as a fuel for household heating and cooking [37,38]. The Japanese government is anticipating a dimethyl ether infrastructure by the end of the decade.

The storage and handling of dimethyl ether 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 dimethyl ether. In addition, the existing natural gas infrastructure can be used to distribute DME. Consequently, dimethyl ether is a promising alternative fuel for generating hydrogen-rich fuel-cell feeds.

1.1. Scope

This paper reports the results of thermodynamic equilibrium composition calculations of the production of hydrogen-rich fuel-cell feeds by dimethyl ether steam reforming. This research augments the work published by Sobyani et al. [5] who investigated the effects of temperature (327–727 °C), pressure (1–5 atm) and steam-to-carbon ratio (0.5–10) on dimethyl ether steam reforming. Our study expands upon the previous research by examining lower temperatures (100–600 °C) and expanding the product set to consist of hydrogen, carbon monoxide, carbon dioxide, acetylene, ethanol, methanol, ethylene, methyl-ethyl ether, formaldehyde, formic acid, acetone, *n*-propanol, ethane, and isopropyl alcohol. Also, the equilibrium product compositions resulting from the production of methanol by the hydrolysis of dimethyl ether were investigated as a function of temperature (100–600 °C) and steam-to-carbon ratio (0.00–5.00). Details of the calculations and the tabulated results for both dimethyl ether steam reforming and dimethyl ether hydrolysis can be found in LA-14166 at <http://www.osti.gov/bridge/>. This report is available upon request.

2. Modeling methodology

2.1. Gibb's free energy

Equilibrium compositions were calculated by the minimization of the Gibb's free energy. The Gibb's free energy equations that were minimized are shown in Eq. (1). A derivation of these equations is given in Perry's Chemical Engi-

neers' Handbook [39]:

$$\Delta G_{\text{fi}}^{\circ} + RT \ln P + RT \ln y_i + RT \ln \hat{\phi}_i + \sum_k \lambda_k a_{ik} = 0, \quad (1)$$

subject to the constraints:

$$\sum_i y_i a_{ik} = A_k / \sum_i n_i \quad \text{and} \quad \sum_i y_i = 1,$$

where $\Delta G_{\text{fi}}^{\circ}$ is the standard Gibbs function of formation of compound *i*, *R* the molar gas constant, *T* the processing temperature, *P* the processing pressure, *y_i* the gas phase mole fraction of compound *i*, $\hat{\phi}_i$ the fugacity coefficient of compound *i*, λ_k the Lagrange multiplier, *a_{ik}* the number of atoms for *k*th elements of species *i*, *A_k* the total mass of *k*th element and *n_i* the moles of compound *i*. All equilibrium calculations were performed with vapor phase constituents. The equation of state used was the Peng–Robinson equation. Minimization was accomplished with Aspen Tech™, commercial software capable of performing multicomponent equilibria.

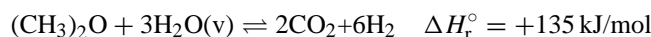
The modeling methodology is represented by the flow chart in Fig. 1. There are four steps to calculate chemical equilibrium:

1. choose reactants and their relative proportions;
2. choose products;
3. choose processing temperature and pressure;
4. perform minimization.

2.2. Dimethyl ether steam reforming

The primary reactions and temperatures chosen for the initial equilibrium modeling were based on experimental observations [9]. The reactions or constrained equilibria are: The primary reactions and temperatures chosen for the initial equilibrium modeling were based on experimental observations [9]. The reactions or constrained equilibria are:

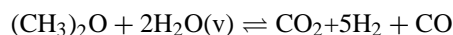
DME steam reforming :



Water-gas shift :



Net reaction :



$$\Delta H_{\text{r}}^{\circ} = +176 \text{ kJ/mol}$$

Both reactions are endothermic in the forward direction. Dimethyl ether steam reforming requires approximately three times the energy as the forward water-gas shift reaction. The sum of the two equations, results in a composite reaction with a large endothermic enthalpy, 176 kJ mol⁻¹. The composite reaction was taken as the product basis set (CH₃OCH₃, H₂O, CO₂, CO, H₂). The temperature and pres-

sure ranges investigated were 100–600 °C and 1–5 atm, respectively, with steam-to-carbon ratios ranging from 0.00 to 4.00.

Given the processing temperatures and products, the equilibrium compositions were calculated. The equilibrium compositions were mapped for each condition, and the optimal processing temperature and feed composition were deter-

mined. The processing pressure was then varied to ascertain its effects on the equilibrium composition.

2.3. DME-SR: thermodynamically plausible products

Depending on the operating conditions and catalysts employed, the product composition may be different from

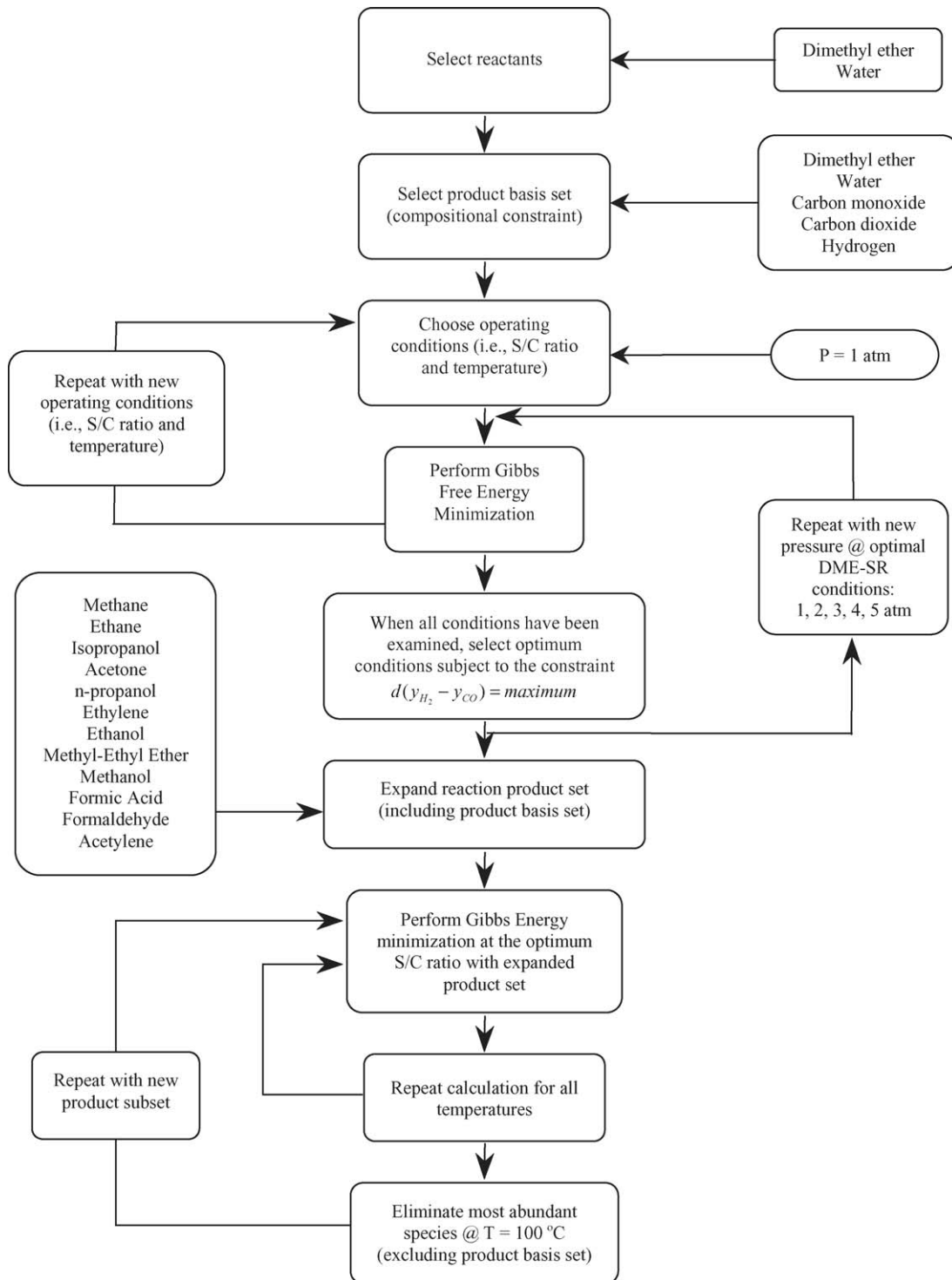


Fig. 1. DME-SR modeling methodology flow chart.

Table 1
Expanded DME-SR product set at optimal processing conditions

Expanded product set	
Acetone	Formic acid
Acetylene	Hydrogen ^a
Carbon dioxide ^a	Isopropanol
Carbon monoxide ^a	Methane
Dimethyl ether (DME) ^a	Methanol
Ethane	Methyl-ethyl ether
Ethanol	<i>n</i> -Propanol
Ethylene	Water ^a
Formaldehyde	

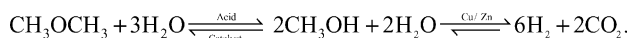
^a Product basis set.

those assumed above (CH₃OCH₃, H₂O, CO₂, CO, H₂). The product set was expanded to include species that may be intermediates or products formed from side reactions. The expanded product set is shown in Table 1.

To explore additional thermodynamic products under various degrees of selectivity (i.e., compositional constraints), the species with the largest effluent mole fraction at a temperature of 100 °C and a steam-to-carbon ratio of 2.50 was removed from the product set—excluding the products in the basis set, then the calculations were repeated, thus defining a new thermodynamic case study. In all cases, the product sets did not include carbon as a thermodynamically viable species. Carbon was excluded because the rate of carbon formation has been observed in experiments to be slow [10,11].

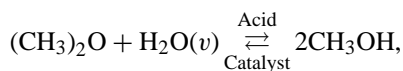
2.4. Dimethyl ether hydrolysis

The process of dimethyl ether steam reforming over acid catalysts is observed to proceed by a two step reaction sequence, where dimethyl ether is first converted to methanol (dimethyl ether hydrolysis), which is then converted to H₂ and CO₂ by methanol steam reforming [8–11]:



Methanol has also been observed as an intermediate during conversion of syngas to higher molecular weight hydrocarbons [9,14,23,40–47]. This reaction occurs over acid catalysts, where syngas is first converted to methanol and subsequently, methanol equilibrates with dimethyl ether via DME hydrolysis:

DME hydrolysis :



$$\Delta H_r^\circ = +37 \text{ kJ/mol}.$$

The equilibrium product composition was modeled as a function of temperature and steam-to-carbon ratio to identify the limits on conversion. The temperature range investigated was identical to the temperature range used for the process of dimethyl ether steam reforming (100–600 °C). The range of steam-to-carbon ratios was expanded to 0.00–5.00. Because there is no difference in molar quantity between products and reactants in the hydrolysis of dimethyl ether, a change in

pressure will not shift the equilibrium, hence the processing pressure was maintained at 1 atm.

3. Results and discussion

3.1. Dimethyl ether steam reforming

Fig. 2 illustrates the equilibrium conversion of dimethyl ether as a function of steam-to-carbon ratio and temperature. The conversion of DME approaches 1 for all practical operating conditions (i.e., $T > 200$ °C and $S/C > 1.50$). The steam reforming conversion of dimethyl ether is not limited by equilibrium.

Fig. 3 depicts the hydrogen mole fraction on a wet and dry basis for dimethyl ether steam reforming as a function of steam-to-carbon ratio and temperature. The maximum equilibrium hydrogen effluent mole fraction modeled was 0.72 for a steam-to-carbon ratio equal to 1.50 and a temperature of 200 °C. The theoretical maximum mole fraction of hydrogen for dimethyl ether steam reforming is 0.75. The hydrogen production efficiency as a function of temperature and steam-to-carbon ratio is shown in Fig. 3c. Hydrogen production efficiency was defined as the effluent mole fraction of hydrogen on a wet basis divided by 0.75. The decrease in the hydrogen mole fraction in Fig. 3a and the decrease in the hydrogen production efficiency in Fig. 3c for steam-to-carbon ratios greater than 1.00 are the result of steam dilution (i.e., $S/C > 1.50$).

Given a constant steam-to-carbon ratio, the hydrogen mole fraction decreases monotonically as the temperature increases (Fig. 3a), primarily due to the water-gas shift equilibrium. Accompanying a decrease in the hydrogen mole fraction is an increase in the carbon monoxide concentration.

The hydrogen mole fraction increases with increasing steam-to-carbon ratio because of the increased conversion of dimethyl ether to hydrogen, reaching a maximum at a steam-to-carbon ratio of 1.50, then decreases as the steam-

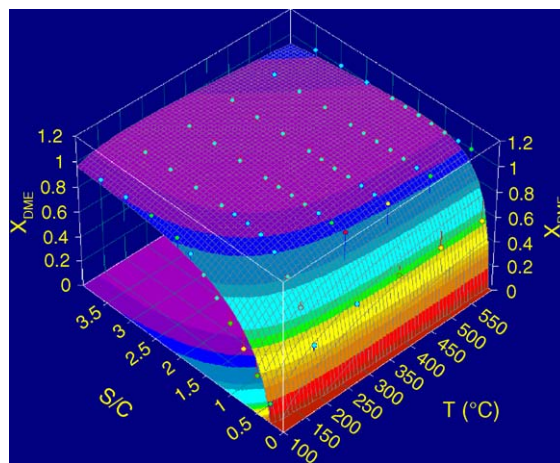


Fig. 2. Plot of the thermodynamic equilibrium conversion of dimethyl ether as a function of steam-to-carbon ratio and temperature.

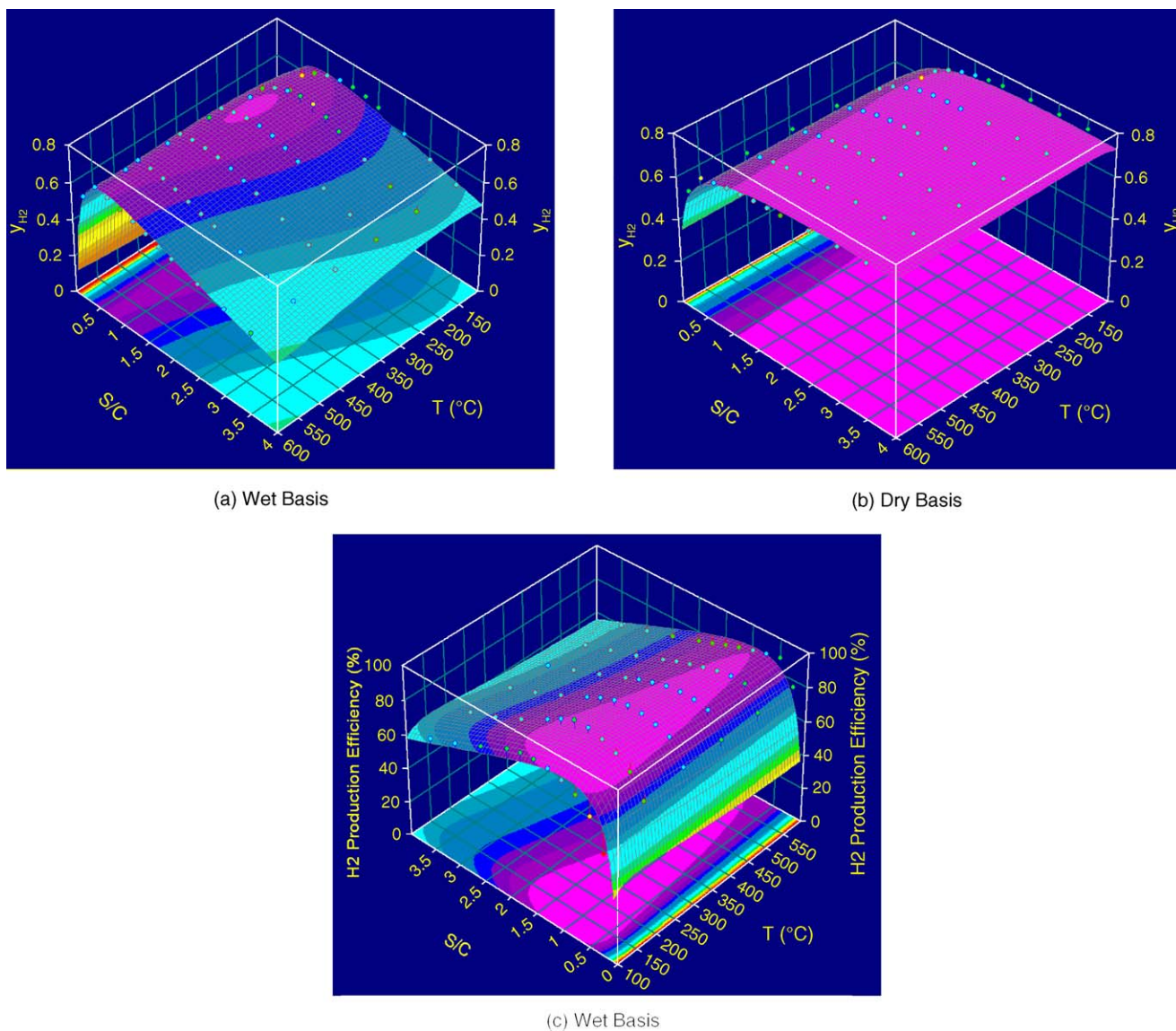


Fig. 3. Plot of the thermodynamic equilibrium product mole fractions of hydrogen on a (a) wet and (b) dry basis as a function of steam-to-carbon ratio and temperature for dimethyl ether-steam reforming; (c) hydrogen production efficiency on a wet basis as a function of steam-to-carbon ratio and temperature.

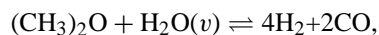
to-carbon ratio is further increased because of steam dilution. The hydrogen mole fraction on a wet basis (Fig. 3a) decreases faster due to steam dilution than the increase in hydrogen production from the water-gas shift reaction (Fig. 3b) as the steam-to-carbon ratio is increased. In a DME-SR fuel processor, high steam-to-carbon ratios will have a larger impact on the reactor volume (due to an increased water influent) and on the reactor heat duty (due to an increase in vaporization energy) than on the carbon monoxide effluent content, as exemplified by the comparison of Fig. 3a and b.

3.2. DME-SR: carbon monoxide product mole fraction

Production of carbon monoxide during the steam reforming of dimethyl ether is attributed to the water-gas shift reac-

tion and the partial steam reforming reaction (PSR):

DME-PSR :



$$\Delta H_{\text{rxn}}^{\circ} = +217 \text{ kJ/mol.}$$

The carbon monoxide product concentration on a wet basis (depicted in Fig. 4a) occurs within a narrow range of steam-to-carbon ratios—indicated by the small radius of curvature at the maximum. The maximum occurs during dimethyl ether partial steam reforming at a steam-to-carbon ratio of 0.50. Steam-to-carbon ratios of less than 1.00 are to be avoided because of the conversion constraint (i.e., <99.5%), thus eliminating the region of global maxima of carbon monoxide. For steam-to-carbon ratios greater than 1.50, the primary re-

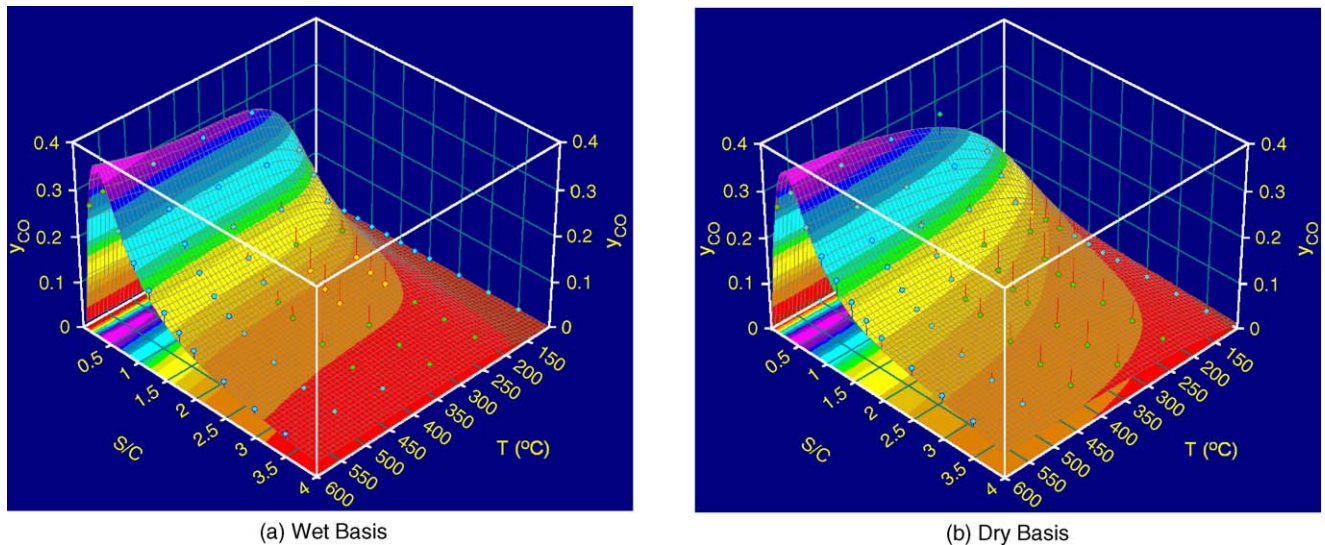


Fig. 4. Plot of the thermodynamic equilibrium-product mole fractions of carbon monoxide on a (a) wet and (b) dry basis as a function of steam-to-carbon ratio and temperature for dimethyl ether steam reforming.

action responsible for carbon monoxide production is the water-gas shift reaction. The carbon monoxide mole fraction is observed to increase with increasing temperature for a given steam-to-carbon ratio and decrease with an increasing steam-to-carbon ratio at a given temperature. There is no mole change with the water-gas shift reaction; therefore, pressure effects are negligible.

3.2.1. DME-SR: optimal processing for PEM fuel cells

The optimal processing of any hydrocarbon fuel for producing hydrogen-rich fuel-cell feeds requires minimization of the carbon monoxide content to maximize the hydrogen content. This assumes that the carbon monoxide effluent is processed using PrOx reactors to a level that preserves the operability of PEM fuel cells, typically ≤ 10 ppm. Minimizing the carbon monoxide content and steam-to-carbon ratio in a steam reforming unit reduces the downstream reactor volumes and proportionately decreases startup energy, thus increasing the overall efficiency of the fuel processor [4]. The objective function used consists of the difference in product compositions of hydrogen and carbon monoxide on a wet basis:

$$d(y_{\text{H}_2} - y_{\text{CO}})_{\text{wet basis}} = 0(\text{maximum})$$

$$\text{given } X_{\text{DME}} \geq 99.5\%.$$

The aim is maximization of this objective function given a dimethyl ether conversion constraint of 99.5%. To identify the optimal operating conditions, the difference in product mole fractions as a function of steam-to-carbon ratio and processing temperature were plotted (Fig. 5). The local maxima of the objective function on a wet basis (Fig. 5a) are shown to encompass small regions of temperature (100–300 °C) and steam-to-carbon ratios (1.25–2.50). This topographical region has a minimum difference of 0.60. The maximum differ-

ence is 0.70 and occurs at a steam-to-carbon ratio of 1.50 and a temperature of 200 °C—this correlates to a hydrogen production efficiency of 97%. The differences in product mole fractions on a dry basis are shown in Fig. 5b.

Comparing Fig. 5a and b illustrate the effects of dilution on the objective function. Plotting the difference in hydrogen and carbon monoxide on a dry basis (Fig. 5b), the suitable processing conditions resulting in a maximum difference expand to include temperatures up to 450 °C and steam-to-carbon ratios up to 4.0. The purpose of plotting the two objective functions is to give a qualitative perspective on the optimal conditions for generating hydrogen-rich fuel-cell feeds with different design constraints. In the case of portable or automotive applications where size, volume and efficiency are critical design constraints, excess water (e.g., $S/C > 2.50$) correlates to larger heat exchangers, increased vaporization energy and increased water storage. For stationary applications, where the size and volume constraints are relaxed, excess water may prove useful.

3.2.2. DME-SR: pressure effects

The optimal steam-to-carbon ratio of 2.50 was chosen to investigate the effects of pressure on dimethyl ether steam reforming and determine the thermodynamically viable products during the process of dimethyl ether steam reforming. The effect of pressure on the fractional concentrations of dimethyl ether and hydrogen at a temperature of 100 °C and a steam-to-carbon ratio of 2.50 is depicted in Fig. 6. Increasing the pressure from 1 to 5 atm decreases the hydrogen production efficiency by 12% and decreases dimethyl ether conversion by 23%. Increasing the pressure shifts the equilibrium to the reactants, hence dimethyl ether steam reforming should be operated at low pressures to maintain a high degree of hydrogen production efficiency.

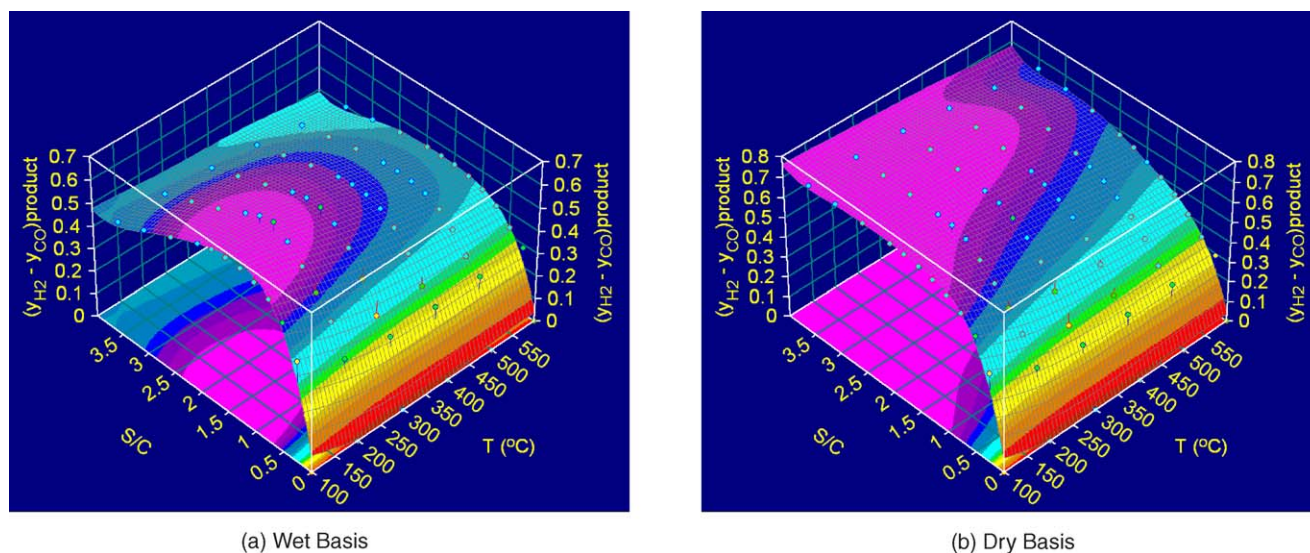


Fig. 5. Plot of the difference in thermodynamic equilibrium product mole fractions of hydrogen and carbon monoxide on (a) wet and (b) dry basis as a function of steam-to-carbon ratio and temperature for dimethyl ether-steam reforming.

3.2.3. DME-SR: thermodynamically plausible products

A steam-to-carbon ratio of 2.50 (Fig. 5a) and a pressure of 1 atm (Fig. 6) were chosen as the operating conditions for the determination of additional products. The thermodynamic equilibrium compositions were determined for operating temperatures ranging from 100 to 600 °C. The thermodynamically favored species in order of decreasing effluent mole fraction are tabulated in Table 2. While the trend in Table 2 was tabulated for a steam-to-carbon ratio of 2.50, it will be observed for all steam-to-carbon ratios. However, the equilibrium product concentrations will be different.

Given the products considered, methane (case 1) was the most abundant and methanol (case 10) the least abundant. The fractional concentrations of the most abundant species

as a function of temperature are shown in Fig. 7. Methane is favored over the entire temperature range investigated, while ethane is favored in the range of 100–500 °C, when methane is not considered. For cases 3–8 the products approach zero fractional concentration as the temperature approaches 300 °C. Methanol, case 9, is observed, but with a concentration of about 900 ppm at a temperature of 100 °C. The absence of significant amounts of methanol is a direct consequence of the product basis set (specifically hydrogen, carbon dioxide and carbon monoxide). Similarly, formic acid, formaldehyde and acetylene were not observed to be favored thermodynamically. Although some of the species in the expanded product set are favored thermodynamically at defined operating conditions, they may not be observed experimen-

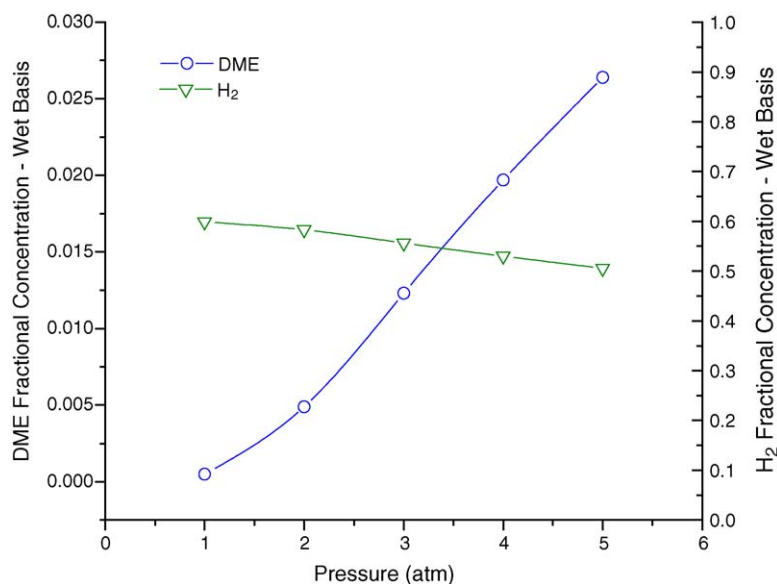


Fig. 6. Pressure effects on DME-SR compositions of hydrogen and dimethyl ether processed at a temperature of 100 °C and a steam-to-carbon ratio of 2.5.

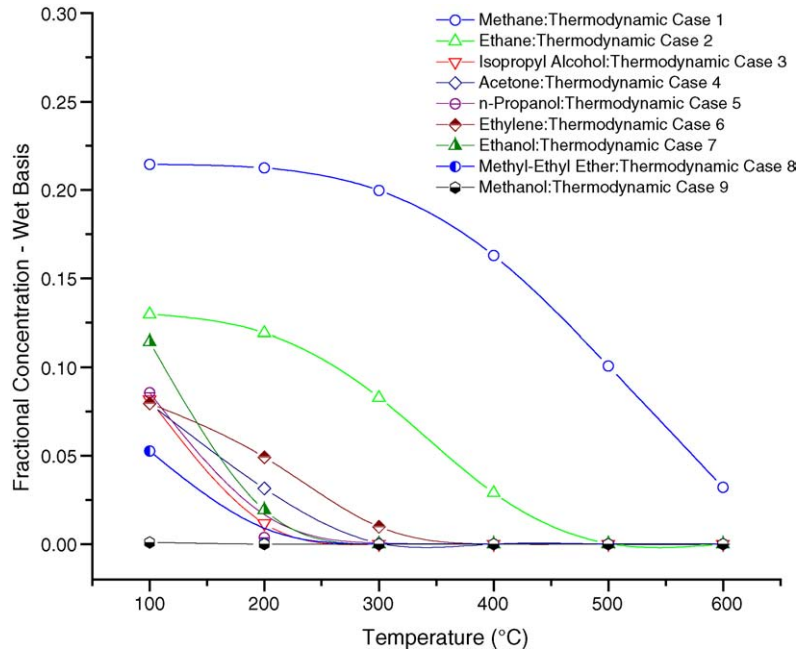


Fig. 7. Compositions of the most abundant species for thermodynamic cases 1–9 as a function of temperature at a steam-to-carbon ratio of 2.5 and a pressure of 1 atm.

tally. The catalysts employed will determine product selectivity.

3.3. Dimethyl ether hydrolysis

The conversion of dimethyl ether through hydrolysis to methanol as a function of steam-to-carbon ratio and temperature is depicted in Fig. 8. For this case, the only species considered were DME, methanol and water. The conversion of dimethyl ether to methanol is limited by equilib-

rium. Dimethyl ether conversion increases monotonically with increasing steam-to-carbon ratio at a given temperature and increasing temperature at a given steam-to-carbon ratio. Increasing both the processing temperature and steam-to-carbon ratio, results in the maximum increase in dimethyl ether conversion to methanol.

For a stoichiometric steam-to-carbon ratio (e.g., 0.50), the highest conversion of dimethyl ether that can be reached in the temperature range investigated is 25% at 600 °C. At a steam-to-carbon ratio of 2.00 the conversion of dimethyl ether is 26% at 300 °C. The maximum conversion of dimethyl ether (e.g., 62%) occurs at the extrema ($T = 600\text{ °C}$ and $S/C = 5.00$).

Table 2

Thermodynamic cases for expanded dimethyl ether steam reforming product set with steam-to-carbon ratio of 2.5 and a pressure of 1 atm

Thermo case	Most abundant	Species excluded
1	Methane	None
2	Ethane	Methane
3	Isopropyl alcohol	Ethane + methane
4	Acetone	Isopropyl alcohol + ethane + methane
5	<i>n</i> -Propanol	Acetone + isopropyl alcohol + ethane + methane
6	Ethylene	<i>n</i> -Propanol + acetone + isopropyl alcohol + ethane + methane
7	Ethanol	Ethylene + <i>n</i> -propanol + acetone + isopropyl alcohol + ethane + methane
8	Methyl-ethyl ether	Ethanol + ethylene + <i>n</i> -propanol + acetone + isopropyl alcohol + ethane + methane
9	Methanol	Methyl-ethyl ether + ethanol + ethylene + <i>n</i> -propanol + acetone + isopropyl alcohol + ethane + methane

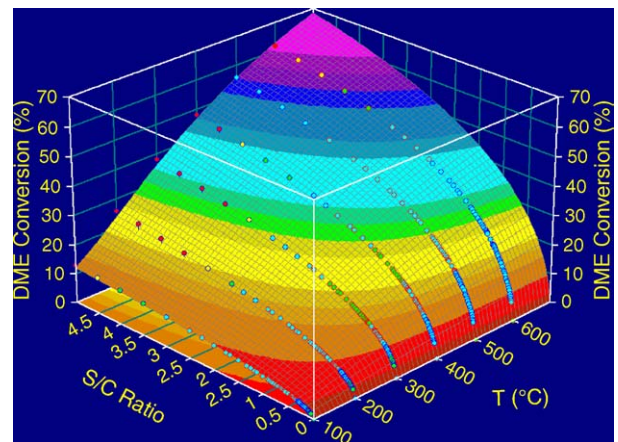


Fig. 8. DME equilibrium conversion as a function of temperature and steam-to-carbon ratio for the hydrolysis of dimethyl ether.

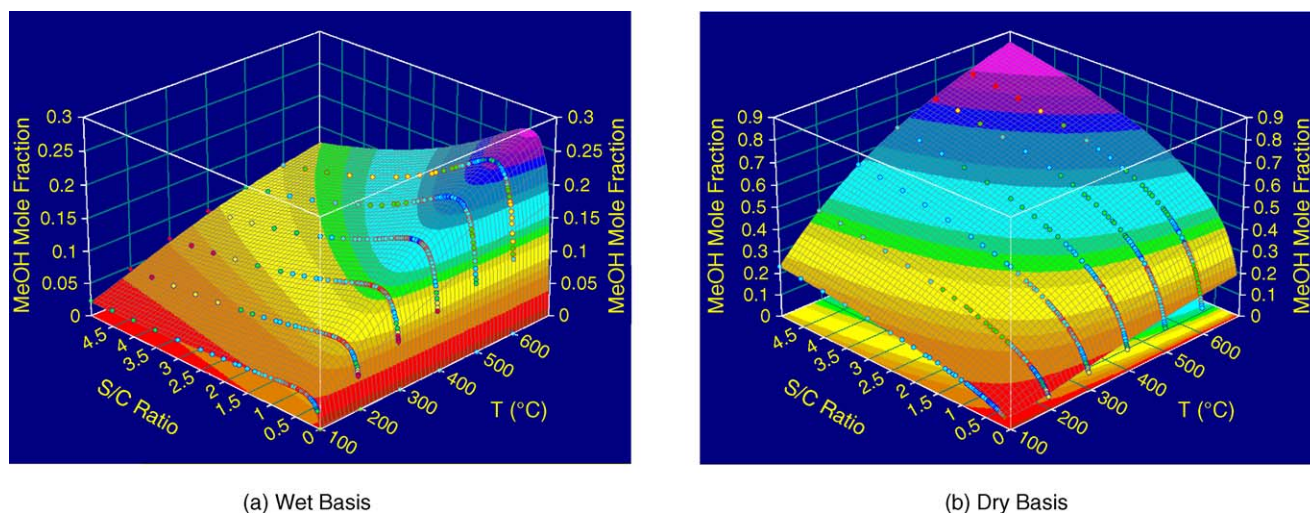


Fig. 9. Effluent equilibrium compositions of methanol on a (a) wet and (b) dry basis as a function of temperature and steam-to-carbon ratio for the hydrolysis of dimethyl ether.

The equilibrium methanol composition for dimethyl ether hydrolysis as a function of steam-to-carbon ratio and temperature is illustrated in Fig. 9. At a given steam-to-carbon ratio, the methanol mole fraction on a wet basis (Fig. 9a) is nonmonotonic with increasing temperature, while it is monotonic on a dry basis (Fig. 9b). The nonmonotonic nature of the methanol effluent mole fraction as a function of the steam-to-carbon ratio is a direct consequence of steam dilution. The maximum methanol effluent mole fraction on a wet basis occurs at a steam-to-carbon ratio of 1.00 and a temperature of 600 °C with a value equaling 23%, while on a dry basis the maximum methanol effluent mole fraction occurs at the extrema ($T = 600$ °C and $S/C = 5.00$) at 85%. Increasing the steam-to-carbon ratio introduces water into the system faster than the increase in the equilibrium composition of methanol; evidenced by comparing Fig. 9a and b.

4. Conclusions

This study focused on the thermodynamic aspects of generating hydrogen-rich fuel-cell feeds from dimethyl ether steam reforming and the thermodynamics of dimethyl ether hydrolysis. The compositions of dimethyl ether steam reforming were determined as a function of temperature (100–600 °C), steam-to-carbon ratio (0.00–4.00), pressure (1–5 atm) and product species. Dimethyl ether hydrolysis was investigated as a function of temperature (100–600 °C) and steam-to-carbon ratio (0.00–5.00) at a pressure of 1 atm.

Based on the results the following conclusions were drawn:

- Thermodynamically, dimethyl ether processed with steam generates hydrogen-rich fuel-cell feeds over a range of temperatures (200–600 °C), steam-to-carbon ratios (1.25–4.00) and pressures (1–5 atm). The maximum hy-

drogen production efficiency of 97% occurs at a steam-to-carbon ratio of 1.50, a temperature of 200 °C and a pressure of 1 atm.

- The conversion of dimethyl ether to hydrogen, carbon monoxide and carbon dioxide is not limited by equilibrium for temperatures greater than 200 °C and steam-to-carbon ratios greater than 1.25 at 1 atm.
- Increasing the pressure from 1 to 5 atm decreases the conversion of dimethyl ether from 99.5 to 76.2%.
- If the catalysts employed are not selective toward hydrogen, carbon monoxide and carbon dioxide, then additional thermodynamically stable products are observed. The order of thermodynamically stable products in decreasing mole fraction is methane, ethane, isopropyl alcohol, acetone, *n*-propanol, ethylene, ethanol, methyl-ethyl ether and methanol. Formaldehyde, acetylene and formic acid are not thermodynamically favored.
- Methanol produced from the hydrolysis of dimethyl ether is thermodynamically limited. Equilibrium conversion increases with temperature and steam-to-carbon ratio. The maximum conversion of dimethyl ether occurs at the extrema ($T = 600$ °C and $S/C = 5.00$) correlating to a value of 62%.
- The ranges of temperature and steam-to-carbon ratio for dimethyl ether steam reforming based on the objective function: $d(y_{H_2} - y_{CO})_{\text{wet basis}} = \text{maximum}$ are 100–300 °C and 1.50–2.50, respectively.

Acknowledgements

This work was partially supported by the US Department of Energy, Hydrogen, Fuel Cells and Infrastructure Program. The authors gratefully acknowledge Michael A. Inbody for his comments and suggestions.

References

- [1] T. Fleisch, Proceedings of the IBC Gas to Liquids Conference, Milan, Italy, 2002.
- [2] J.T. Muller, P.M. Urban, W.F. Holderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, *J. Electrochem. Soc.* 147 (2000) 4058–4060.
- [3] E.P. Murray, S.J. Harris, H.W. Jen, *J. Electrochem. Soc.* 149 (2002) A1127–A1131.
- [4] T.A. Semelsberger, L.F. Brown, R.L. Borup, M.A. Inbody, *Int. J. Hydrogen Energy* 29 (2004) 1047–1064.
- [5] V.A. Sobyenin, S. Cavallaro, S. Freni, *Energy Fuels* 14 (2000) 1139–1142.
- [6] S.Z. Wang, T. Ishihara, Y. Takita, *Electrochem. Solid State Lett.* 5 (2002) A177–A180.
- [7] Yomada, Koji, Asazawa, Koichiro, Tanaka, Hirohisa, Dimethyl ether reforming catalyst, Daihatsu Motor Co., Ltd., 653362 [6,605,559] (2003).
- [8] Bhattacharyya, Alakananda, Basu, Arunabha, Process for hydroshifting dimethyl ether, Amoco Corporation, 356492 [5,498,370] (1996).
- [9] T.A. Semelsberger, R.L. Borup, Proceedings of the 205th Electrochemical Society Meeting, San Antonio, TX, 2004.
- [10] V.V. Galvita, G.L. Semin, V.D. Belyaev, T.M. Yurieva, V.A. Sobyenin, *Appl. Catal. A: Gen.* 216 (2001) 85–90.
- [11] T.A. Semelsberger, R.L. Borup, J.I. Tafuya, Proceedings of the Fuel Cell Seminar, San Antonio, TX, 2004.
- [12] F.J. Keil, *Micropor. Mesopor. Mater.* 29 (1999) 49–66.
- [13] T. Shikada, Y. Ohno, T. Ogawa, M. Ono, M. Mizuguchi, K. Tomura, K. Fujimoto, *Stud. Surf. Sci. Catal.* 119 (1998) 515–520.
- [14] M. Stocker, *Micropor. Mesopor. Mater.* 29 (1999) 3–48.
- [15] X.M. Zheng, J.H. Fei, Z.Y. Hou, *Chin. J. Chem.* 19 (2001) 67–72.
- [16] J. Haggin, *Chem. Eng. News* 69 (1991) 20–21.
- [17] H.J. Kim, H. Jung, K.Y. Lee, *Kor. J. Chem. Eng.* 18 (2001) 838–841.
- [18] X.D. Peng, A.W. Wang, B.A. Toseland, P.J.A. Tijm, *Ind. Eng. Chem. Res.* 38 (1999) 4381–4388.
- [19] G.X. Qi, J.H. Fei, X.M. Zheng, Z.Y. Hou, *React. Kinet. Catal. Lett.* 73 (2001) 245–256.
- [20] W.J. Shen, K.W. Jun, H.S. Choi, K.W. Lee, *Kor. J. Chem. Eng.* 17 (2000) 210–216.
- [21] T. Shikada, Y. Ohno, T. Ogawa, M. Ono, M. Mizuguchi, K. Tomura, K. Fujimoto, *Kinet. Catal.* 40 (1999) 395–400.
- [22] Z.L. Wang, J. Diao, J.F. Wang, Y. Jin, X.D. Peng, *Chin. J. Chem. Eng.* 9 (2001) 412–416.
- [23] M. Xu, J.H. Lunsford, D.W. Goodman, A. Bhattacharyya, *Appl. Catal. A: Gen.* 149 (2) 289–301.
- [24] N. Elam, The Bio-DME Project, 2002.
- [25] T.H. Fleisch, A. Basu, M.J. Gradassi, J.G. Masin, *Stud. Surf. Sci. Catal.* 107 (1997) 117–125.
- [26] D.W. Gill, 9th IEA Workshop, Paris, 2001.
- [27] J.B. Hansen, S. Mikkelsen, DME as a transportation fuel, 2001.
- [28] Z.H. Huang, H.W. Wang, H.Y. Chen, L.B. Zhou, D.M. Jiang, *Proc. Inst. Mech. Eng. D: J. Automob. Eng.* 213 (1999) 647–652.
- [29] International Energy Agency, Dimethyl ether as automotive fuel, DME Newsletter 3, 1999.
- [30] International Energy Agency, Dimethyl ether as automotive fuel, DME Newsletter 4, 2000.
- [31] M.M. Roy, H. Tsunemoto, H. Ishitani, *JSME Int. J. Ser. B: Fluids Therm. Eng.* 43 (2000) 511–517.
- [32] H.W. Wang, Z.H. Huang, L.B. Zhou, D.M. Jiang, Z.L. Yang, *Proc. Inst. Mech. Eng. D: J. Automob. Eng.* 214 (2000) 503–508.
- [33] H.W. Wang, L.B. Zhou, D.M. Jiang, Z.H. Huang, *Proc. Inst. Mech. Eng. D: J. Automob. Eng.* 214 (2000) 101–106.
- [34] E.M. Chapman, S.V. Bhide, A.L. Boehman, L.I. Boehman, F. Waller, Proceedings of the Spring National Meeting, New Orleans, LA, 2002.
- [35] Z.L. Chen, M. Konno, S. Kajitani, *JSME Int. J. Ser. B: Fluids Therm. Eng.* 43 (2000) 82–88.
- [36] A.M. Rouhi, *Chem. Eng. News* 73 (1995) 37–39.
- [37] M. Sun, L. Yu, C. Sun, Y. Song, J. Sun, *Gen. Rev.* 20 (2003).
- [38] Y. Ohno, N. Inoue, T. Ogawa, M. Ono, T. Shikada, H. Hayashi, NKK Technical Review, 2001.
- [39] R.H. Perry, D.W. Green, J.O. Maloney, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, New York, 1999.
- [40] J. Bandiera, C. Naccache, *Appl. Catal.* 69 (1991) 139–148.
- [41] D. Freeman, R.P.K. Wells, G.J. Hutchings, *J. Catal.* 205 (2002) 358–365.
- [42] G.J. Hutchings, G.W. Watson, D.J. Willock, *Micropor. Mesopor. Mater.* 29 (1999) 67–77.
- [43] M. Hytha, I. Stich, J.D. Gale, K. Terakura, M.C. Payne, *Chem. A Eur. J.* 7 (2001) 2521–2527.
- [44] K. Klier, A. Beretta, Q. Sun, O.C. Feeley, R.G. Herman, *Catal. Today* 36 (1997) 3–14.
- [45] T.Y. Park, G.F. Froment, *Ind. Eng. Chem. Res.* 40 (2001) 4172–4186.
- [46] T.Y. Park, G.F. Froment, *Ind. Eng. Chem. Res.* 40 (2001) 4187–4196.
- [47] M.T. Xu, D.W. Goodman, A. Bhattacharyya, *Appl. Catal. A: Gen.* 149 (1997) 303–309.