

Thermodynamic evaluation of methanol steam reforming for hydrogen production

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Abstract

Thermodynamic equilibrium of methanol steam reforming (MeOH SR) was studied by Gibbs free minimization for hydrogen production as a function of steam-to-carbon ratio ($S/C = 0\text{--}10$), reforming temperature ($25\text{--}1000\text{ }^\circ\text{C}$), pressure ($0.5\text{--}3\text{ atm}$), and product species. The chemical species considered were methanol, water, hydrogen, carbon dioxide, carbon monoxide, carbon (graphite), methane, ethane, propane, *i*-butane, *n*-butane, ethanol, propanol, *i*-butanol, *n*-butanol, and dimethyl ether (DME). Coke-formed and coke-free regions were also determined as a function of S/C ratio.

Based upon a compound basis set MeOH, CO_2 , CO, H_2 and H_2O , complete conversion of MeOH was attained at $S/C = 1$ when the temperature was higher than $200\text{ }^\circ\text{C}$ at atmospheric pressure. The concentration and yield of hydrogen could be achieved at almost 75% on a dry basis and 100%, respectively. From the reforming efficiency, the operating condition was optimized for the temperature range of $100\text{--}225\text{ }^\circ\text{C}$, S/C range of $1.5\text{--}3$, and pressure at 1 atm. The calculation indicated that the reforming condition required from sufficient CO concentration ($<10\text{ ppm}$) for polymer electrolyte fuel cell application is too severe for the existing catalysts ($T_r = 50\text{ }^\circ\text{C}$ and $S/C = 4\text{--}5$). Only methane and coke thermodynamically coexist with H_2O , H_2 , CO, and CO_2 , while C_2H_6 , C_3H_8 , *i*- C_4H_{10} , *n*- C_4H_{10} , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$, *i*- $\text{C}_4\text{H}_9\text{OH}$, *n*- $\text{C}_4\text{H}_9\text{OH}$, and $\text{C}_2\text{H}_6\text{O}$ were suppressed at essentially zero. The temperatures for coke-free region decreased with increase in S/C ratios. The impact of pressure was negligible upon the complete conversion of MeOH.

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1. Introduction

Hydrogen is regarded as a primary energy carrier in the future by virtue of the fact that it can be produced from renewable sources such as biomass, solar energy, and so on, and is efficiently converted to electricity by fuel cells. Polymer electrolyte fuel cells (PEFCs) have presently attracted much attention worldwide since it provides high efficiency with clean exhaust gas by consuming hydrogen and oxygen [1–3]. Development of hydrogen production has been widely studied to commercialize the production process. Reforming of fuels, such as, methanol [4–7], ethanol [8–11], gasoline [12,13], biogas [14,15], natural gas [16–19], and dimethyl ether [20–23], has been developed

for hydrogen production. Steam reforming (SR), partial oxidation (PO), and autothermal steam reforming (ATR) are the major processes for reforming of those fuels. PO and ATR processes have a merit on fast start-up time because of exothermic nature of oxidation reaction. However, the PO and ATR processes provide lower efficiency and reformat quality, i.e., lower hydrogen production yield, higher rate of side reactions, and by-products. SR process gives high concentration of hydrogen ca. 70–80% on a dry basis, while those for PO and ATR are estimated to be ca. 40–50% on a dry basis.

MeOH appears to be a suitable liquid fuel for on-board hydrogen production. Steam reforming of methanol has widely been developed. Generally, MeOH SR can be operated at low temperature of $250\text{--}300\text{ }^\circ\text{C}$. Natural gas and biogas can be reformed at relatively high temperature of $600\text{--}800\text{ }^\circ\text{C}$. These fuels normally contain sulfur compounds that can poison reforming catalysts. Thus, a desulfurizer unit is needed for the reforming system.

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Nomenclature

a_{ik}	number of atoms of the k th element present in each molecule of species i
A_k	total mass of k th element in the feed
\hat{f}_i	the fugacity of species i in system
f_i^0	the standard-state fugacity of species i
F_{H_2out}	molar flow rate of hydrogen at outlet
F_{MeOHin}	molar flow rate of MeOH at inlet
$F_{MeOHout}$	molar flow rate of MeOH at outlet
$G_{C(S)}$	molar Gibbs free energy of solid carbon
$\bar{G}_{C(g)}$	partial molar Gibbs free energy of gas carbon
$\bar{G}_{C(S)}$	partial molar Gibbs free energy of solid carbon
\bar{G}_i	partial molar Gibbs free energy of species i
G^t	total Gibbs free energy
G_i°	standard Gibbs free energy of species i
$\Delta G_{f_i}^\circ$	standard Gibbs function of formation of species i
$\Delta G_{f_{C(S)}}^\circ$	standard Gibbs function of formation of solid carbon
n_c	mole of carbon
N	number of species in the reaction system
P	pressure of system
P^0	standard-state pressure of 101.3 kPa
R	molar gas constant
T	temperature of system
T_c	temperature at which the first disappearance of carbon was achieved
T_r	reforming temperature
y_i	gas phase mole fraction
<i>Greek symbols</i>	
λ_k	Lagrange multiplier
μ_i	chemical potential of species i
$\hat{\phi}_i$	fugacity coefficient of species i

Methane is definitely considered as a key component of SR of natural gas and biogas. Dimethyl ether (DME) has recently become a promising fuel for hydrogen production to be used in fuel cells. DME provides high H/C ratio, high energy density, and non-toxicity. Like LPG, DME can be easily handled, stored, and transported. Moreover, infrastructure of LPG can be readily adapted for DME because of their similar physical property. Interestingly, DME SR is a two-step reaction namely DME hydrolysis following by MeOH SR. Thermodynamic consideration for many reactions for example DME SR [24,25] and MeOH SR [26] has been used to estimate the equilibrium product distribution as a function of the processing conditions. Semelsberger et al. [25] recently calculated the thermodynamic composition using Gibbs free energy minimization method. However, coke formation was not considered in the calculation.

This study presents the thermodynamic equilibrium of hydrogen-rich feed for fuel cell, focusing on steam reforming process of methanol. Influence of steam-to-carbon ratio (S/C = 0–10), reforming temperature (25–1000 °C), and pressure (0.5–3 atm) on conversion of fuels, hydrogen production,

and CO formation has been figured out. Optimal operating conditions of SR processes for hydrogen production were also determined. The wide range of S/C and temperature of MeOH SR was studied in the present paper to find out the optimal operating condition for MeOH SR. Coke formation was also analyzed to determine the coke-formed and coke-free regions. In addition, an effect of pressurized condition on the MeOH reforming performance was investigated for the application to fuel cells.

2. Modeling and simulation methodology

2.1. Minimization of Gibbs free energy

The most commonly used function to identify the equilibrium state is Gibbs free energy. A minimization of total Gibbs free energy is a suitable method to calculate the equilibrium compositions of any reacting system [27]. The total Gibbs free energy of a system is given by the sum of i th species:

$$G^t = \sum_{i=1}^N n_i \bar{G}_i = \sum_{i=1}^N n_i \mu_i = \sum_{i=1}^N n_i G_i^\circ + RT \sum_{i=1}^N n_i \ln \frac{\hat{f}_i}{f_i^0} \quad (1)$$

where G^t is the total Gibbs free energy, \bar{G}_i the partial molar Gibbs free energy of species i , G_i° the standard Gibbs free energy, μ_i the chemical potential, R the molar gas constant, T the temperature of system, P the pressure of system, \hat{f}_i the fugacity in system, f_i^0 the standard-state fugacity, and n_i the mole of species i . For reaction equilibria in gas-phase, $\hat{f}_i = y_i \hat{\phi}_i P$, $f_i^0 = P^0$, and $G_i^\circ = \Delta G_{f_i}^\circ$ are assumed. By using the Lagrange multiplier method, the minimum Gibbs free energy of each gaseous species and that of the total system can be expressed as Eqs. (2) and (3), respectively.

$$\Delta G_{f_i}^\circ + RT \ln \frac{y_i \hat{\phi}_i P}{P^0} + \sum_k \lambda_k a_{ik} = 0 \quad (2)$$

$$\sum_{i=1}^N n_i \left(\Delta G_{f_i}^\circ + RT \ln \frac{y_i \hat{\phi}_i P}{P^0} + \sum_k \lambda_k a_{ik} \right) = 0 \quad (3)$$

with the constraining equation:

$$\sum_i n_i a_{ik} = A_k$$

where $\Delta G_{f_i}^\circ$ is the standard Gibbs function of formation of species i , P^0 the standard-state pressure of 101.3 kPa, y_i the gas phase mole fraction, $\hat{\phi}_i$ the fugacity coefficient of species i , λ_k the Lagrange multiplier, a_{ik} the number of atoms of the k th element present in each molecule of species i , and A_k the total mass of k th element in the feed.

When solid carbon (graphite) is involved in the system, exploiting the vapor–solid phase equilibrium is applied to the Gibbs-energy of carbon as shown in Eq. (4). Substituting Eq. (1) by Eq. (2) for gaseous species and by Eq. (4) for solid species gives the minimization function of Gibbs-energy as following Eq. (5):

$$\bar{G}_{C(g)} = \bar{G}_{C(S)} = G_{C(S)} \cong \Delta G_{f_{C(S)}}^\circ = 0 \quad (4)$$

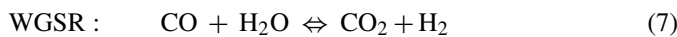
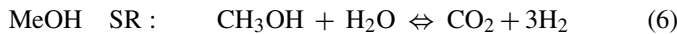
$$\sum_{i=1}^{N-1} n_i \left(\Delta G_{f_i}^{\circ} + RT \ln \frac{y_i \hat{\phi}_i P}{P^0} + \sum_k \lambda_k a_{ik} \right) + (n_c \Delta G_{f_{C(S)}}^{\circ}) = 0 \quad (5)$$

where $\bar{G}_{C(g)}$, $\bar{G}_{C(S)}$, $G_{C(S)}$, $\Delta G_{f_{C(S)}}^{\circ}$ and n_c are the partial molar Gibbs free energy of gas carbon, that of solid carbon, the molar Gibbs free energy of solid carbon, the standard Gibbs function of formation of solid carbon, and mole of carbon, respectively.

The equilibrium calculations employing the Gibbs-energy minimization were done with the Aspen plus, Aspen Tech™. The program is capable to simulate a single phase or multi-phase of multicomponent in equilibria. The steam-to-carbon ratio was varied in the range of 0–10. The reforming temperature T_r and pressure studied were 25–1000 °C, and 0.5–3 atm, respectively. The equation of state used in the calculation was the Soave–Redlich–Kwong method. To perform the calculation, reactant and product species with their proportion along with reaction conditions, i.e., temperature and pressure, have to be clarified. Then, the minimization could be performed to calculate the equilibrium composition. Consecutively, the calculated results were analyzed for an optimal condition of the reforming process.

2.2. MeOH SR

The gas species involved in the MeOH SR are CH₃OH, H₂O, H₂, CO, and CO₂, based on experimental observations [4–7]. The set of other chemical species was considered to determine the plausible products during the steam reforming process. The species considered were carbon (graphite), methane, ethane, propane, *i*-butane, *n*-butane, ethanol, propanol, *i*-butanol, *n*-butanol, and DME. The key reactions concerned in the reforming process are:



The reforming of methanol was performed over Cu/ZnO, Cu/ZnO/Al₂O₃ [4], and Cu/CeO₂/ZrO₃ [5] without the deactivation of the catalysts. Metal catalysts were generally active for water gas shift reaction as well [28–30]. Therefore, the basis set of compounds is acceptable for practical condition.

To evaluate the performance of the steam reforming system, the equilibrium conversions of MeOH, and H₂ yield are defined as follows:

Equilibrium conversion of MeOH (%)

$$= \frac{F_{\text{MeOHin}} - F_{\text{MeOHout}}}{F_{\text{MeOHin}}} \times 100 \quad (9)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{F_{\text{H}_2\text{out}}}{F_{\text{MeOHin}}} \left[\frac{\text{MeOH}}{\text{H}_2} \right]_T \times 100 \quad (10)$$

where F_{MeOHin} and F_{MeOHout} are the molar flow rates of MeOH at inlet and outlet, respectively, and $F_{\text{H}_2\text{out}}$ is molar flow rate of

hydrogen at outlet. $[\text{MeOH}/\text{H}_2]_T$ (1/3) is the theoretical mole ratio of MeOH fed and hydrogen produced.

3. Results and discussion

3.1. Methanol steam reforming: MeOH conversion

Fig. 1 shows the conversion of MeOH as a function of S/C and temperature at 1 atm. As a result, the complete conversion of MeOH was achieved as the temperature and S/C are higher than 200 °C and 1, respectively. At S/C=2, the conversion reached almost 100% even at 100 °C. For S/C lower than 1, MeOH conversion was reduced steeply at the temperatures lower than 200 °C. At S/C=0, the sole reaction is MeOH decomposition providing complete conversion of MeOH while hydrogen concentration reach a maximum at 66.7% on a wet basis (shown in Fig. 2a). Even at S/C < 1, complete conversion of MeOH proceeded with concomitant contribution of steam reforming and decomposition of MeOH.

3.2. Methanol steam reforming: hydrogen production

Fig. 2 illustrates the equilibrium concentration of hydrogen on a wet and a dry basis as a function of S/C and temperature. The hydrogen concentration on a wet basis (Fig. 2a) was maximized to 73.2% with a MeOH conversion of 98.8% at S/C = 1, $T_r = 150$ °C. Since the concentration upper limit assuming reaction (6) is 75%, MeOH SR solely took place at this condition. The MeOH conversion was raised up to 99.9% when the temperature was raised up to 200 °C. However, hydrogen concentration went down to 72.4%. Upon complete MeOH conversion at a given S/C ratio, the hydrogen concentration decreased monotonously as the reforming temperature increased. Meantime, CO concentration monotonously increased, corresponding to the decrease in hydrogen concentration. Evidently, this

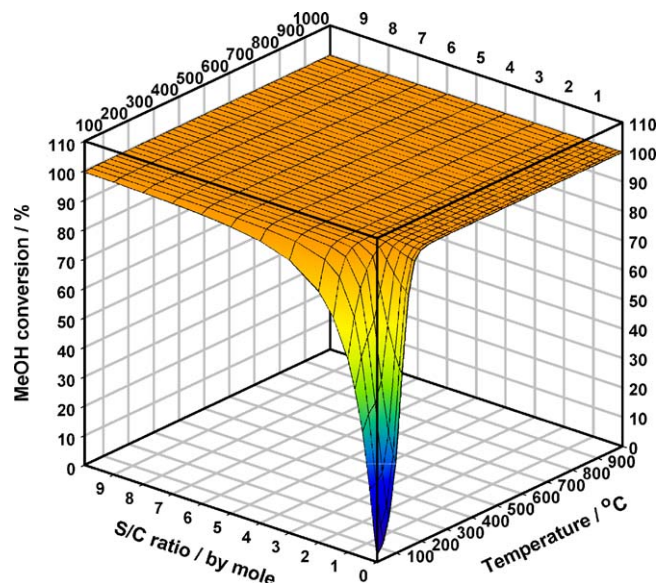


Fig. 1. Equilibrium conversion of MeOH from MeOH SR as a function of steam-to-carbon (S/C) and temperature.

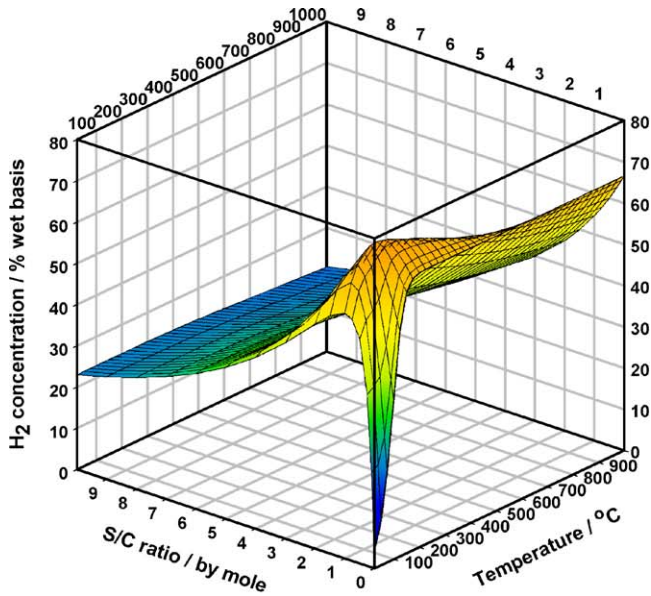
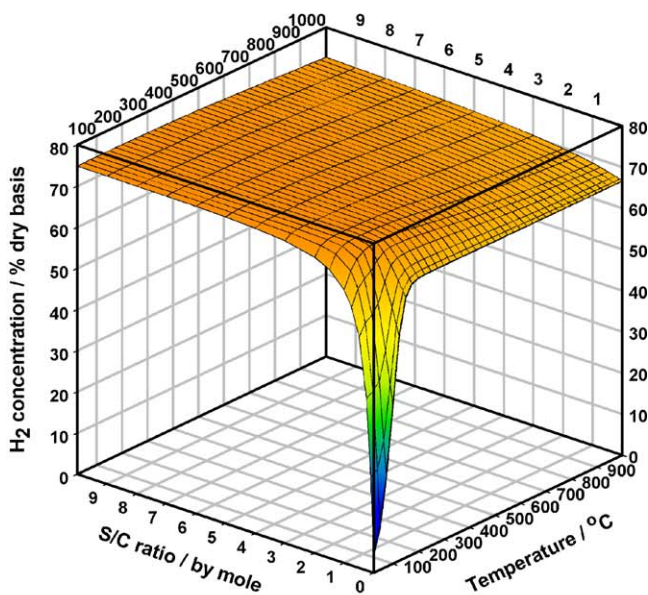
(a) H₂ conc. on a wet basis(b) H₂ conc. on a dry basis

Fig. 2. Equilibrium hydrogen concentration on: (a) wet basis and (b) dry basis from MeOH SR as a function of steam-to-carbon (S/C) and temperature.

should be ascribed by the reverse water gas shift reaction (r-WGSR). The r-WGSR expedites the consumption of hydrogen, and is thermodynamically favorable with increasing temperature. The increase in hydrogen concentration at low S/C was due to the increase of MeOH conversion, approaching a maximum at S/C = 1. The hydrogen concentration subsequently decreased with the increase in S/C on account of dilution with excessive steam. It should be noted that the equilibrium concentration of hydrogen provided by a sole reaction of MeOH decomposition (S/C = 0) was maximum at 66.7% on a dry basis.

The effect of steam dilution was excluded by considering the hydrogen concentration on a dry basis as shown in Fig. 2b. The equilibrium hydrogen concentration could reach maximum of ca. 75% at S/C = 1.5, $T_r = 100\text{--}250\text{ }^\circ\text{C}$, when the expected concentration from reaction (6) was 75% on a dry basis upon complete conversion of MeOH. The temperature range with the maximized hydrogen concentration was widely spread by increasing S/C; i.e., at 75–300 °C for S/C = 2 and at 50–350 °C for S/C = 3. Similar to the concentration on a wet basis, hydrogen concentration markedly increased with an increase in S/C ratio from 0–1. Further increase in S/C still gently raised the hydrogen concentration, since the MeOH conversion was exhibited and r-WGSR was inhibited. Given a fixed S/C at complete MeOH conversion, hydrogen concentration decreased as the temperature increased. The maximum concentration as theoretical value was obtained on a dry basis analysis although it could not be seen on a wet basis due to the effect of steam dilution.

The hydrogen yield from MeOH SR in Fig. 3 approached to 100% with increasing S/C and kept almost constant at 100% with a further increase in S/C when the temperature was in the range of ca. 100–400 °C. In higher temperature range, increasing steam-to-carbon monotonically increased the H₂ yield due to enhancement of MeOH conversion and to suppression of the reverse water gas shift reaction.

3.3. Methanol steam reforming: CO formation

Equilibrium concentration of CO on a wet and a dry basis as a function of S/C and temperature is shown in Fig. 4. Carbon monoxide has been known as the poisonous species for Pt electrode of low-temperature fuel cell. In addition, CO could be a source of coke formation over steam reforming catalysts. The S/C ratios lower than 1.5 led to relatively high CO concentration, especially at high temperatures due to DME decomposition and r-WGSR. At a given an S/C, an increase in temperature resulted

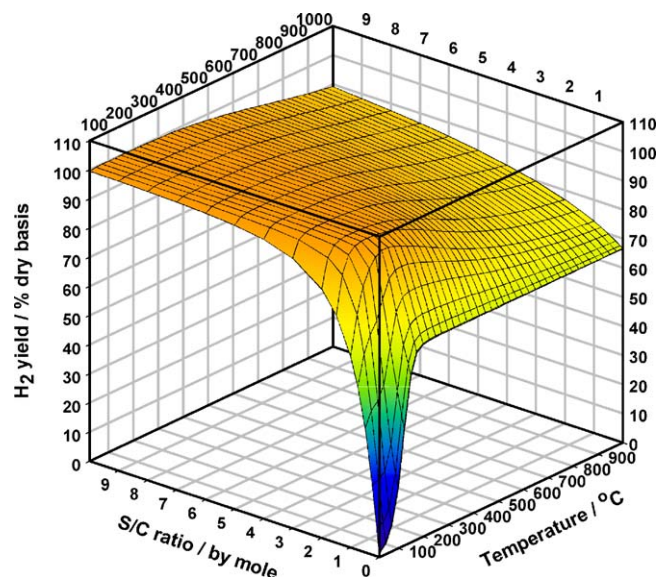
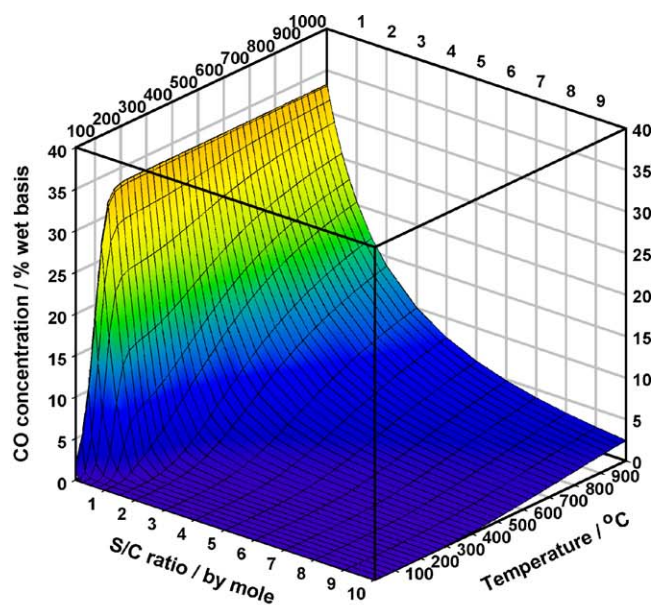
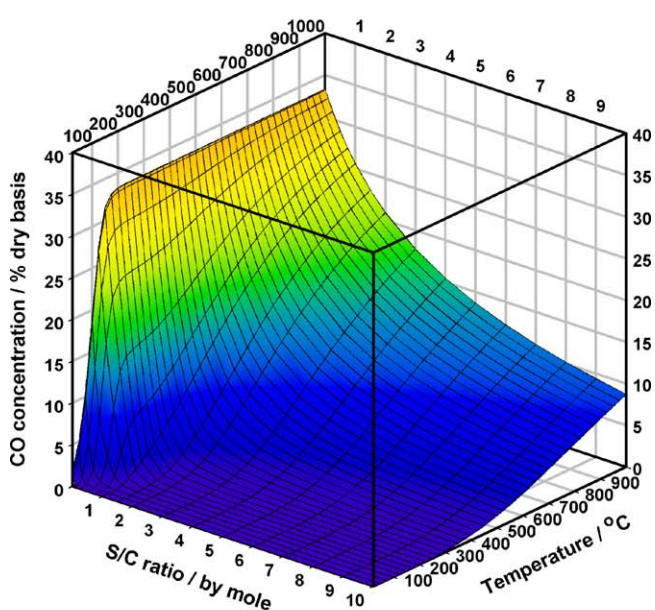


Fig. 3. Equilibrium hydrogen yield from MeOH SR as a function of steam-to-carbon (S/C) and temperature.



(a) CO conc. on a wet basis



(b) CO conc. on a dry basis

Fig. 4. Equilibrium concentration of carbon monoxide on: (a) wet basis and (b) dry basis from MeOH SR as a function of steam-to-carbon (S/C) and temperature.

in an increase in CO. The concentration of CO on a wet basis is lower than that on a dry basis because of dilution with steam.

3.4. Methanol steam reforming: pressure effect

Because of difference in molar quantity between reactants and products, total pressure affected the equilibrium of MeOH SR. Influence of pressure on MeOH SR was investigated for a fixed S/C ratio at 2 and varied temperatures of 25–1000 °C.

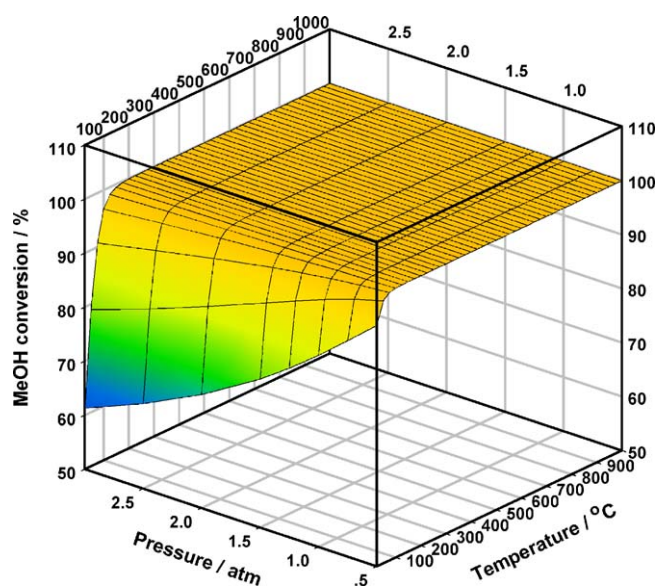


Fig. 5. Equilibrium conversion of MeOH from MeOH SR as a function of pressure and temperature.

Equilibrium MeOH conversion is plotted as a function of pressure and temperature in Fig. 5. At the temperatures higher than ca. 150 °C, pressure from 0.5 to 3 atm had no effect on MeOH conversion, which was already attained 100%. However, at temperatures lower than 150 °C, the conversion was suppressed by increasing pressure. The stronger effect of pressure was found at lower temperatures. Increase in pressure shifts the equilibrium to reactants. The same tendency was observed for hydrogen yield as shown in Fig. 6. At a given pressure, an increase in temperature brought about the drop of hydrogen yield, for the temperature higher than ca. 150 °C. Influence of pressure on CO concentration on a dry basis was shown in Fig. 7. As a result, pressure change from 0.5 to 3 atm did not affect CO concentration, since the overall molar quantity of existing species was

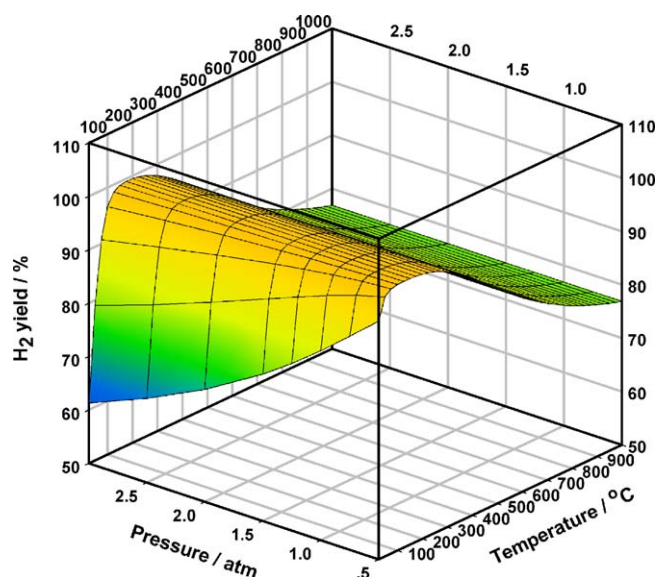


Fig. 6. Equilibrium hydrogen yield of MeOH SR as a function of pressure and temperature.

unchanged with r-WGSR. At a given pressure, CO concentration increased monotonically with increasing temperature. The reaction at about 150–250 °C simultaneously achieved the maximum hydrogen yield and low CO concentration below 1% on a dry basis.

3.5. Methanol steam reforming: thermodynamically plausible products

The equilibrium calculation so far was carried out by taking H_2 , H_2O , CO , CO_2 , and $MeOH$ as existing species. The plausible products in $MeOH$ SR were investigated by adding coke, hydrocarbons or oxygenated compounds into the compound basis set as the following cases:

- Case 1. $MeOH$, H_2O , H_2 , CO , CO_2 , and carbon (graphite).
- Case 2. $MeOH$, H_2O , H_2 , CO , CO_2 , CH_4 , C_2H_6 , C_3H_8 , $i-C_4H_{10}$, $n-C_4H_{10}$, C_2H_5OH , C_3H_7OH , $i-C_4H_9OH$, $n-C_4H_9OH$, and DME.
- Case 3. $MeOH$, H_2O , H_2 , CO , CO_2 , carbon (graphite), and CH_4 .
- Case 4. $MeOH$, H_2O , H_2 , CO , and CO_2 plus each of C_2H_6 , C_3H_8 , $i-C_4H_{10}$, $n-C_4H_{10}$, C_2H_5OH , C_3H_7OH , $i-C_4H_9OH$, $n-C_4H_9OH$, or DME.

An S/C ratio of 2 and a pressure of 1 atm were used as an operating condition. Fig. 8 illustrates the molar fraction of plausible products per mole of $MeOH$ in feed as a function of temperature from 25 to 1000 °C. For Case 1, carbon (graphite), hereafter referred as coke, was produced in the temperature range lower than 500 °C. Coke formation kept essentially constant for the temperatures increase up to 300 °C. Further increase in temperature obviously inhibited the formation of coke. As for Case 2, only methane was thermodynamically stable in the temperature

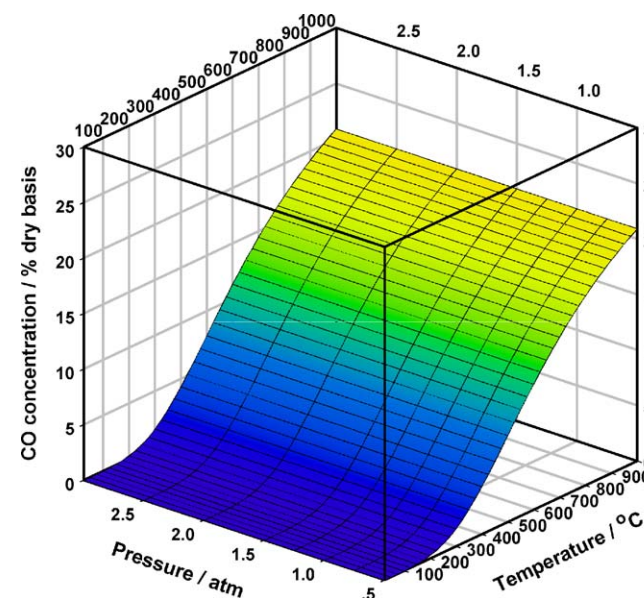


Fig. 7. Equilibrium concentration of carbon monoxide on a dry basis from $MeOH$ SR as a function of pressure and temperature.

range up to 700 °C, while other alkane and oxygen-containing species were suppressed at essentially zero. These alkane and oxygenated species do not coexist in reformat with methane in the whole temperature range. As for Case 3 when coke and methane were simultaneously considered, the methane and coke could coexist at the temperature range below ca. 125 °C. Formation of coke was obviously inhibited by increasing temperature. Only methane was produced at the temperature above 125 °C.

The alkane and oxygenated species are expected to be stable if one does not include methane in the system. On the basis of Case 4, the descending order of the formation of the plausible product is as follows: ethane, propane, *i*-butane or *n*-butane, ethanol, propanol, *i*-butanol or *n*-butanol, and DME, respectively, at the temperatures higher than 150 °C. These alkane, alcohol, and DME species approached zero at ca. 400, 250, and 100 °C, respectively.

In practical cases, methane can be produced from higher carbon-containing alkane, i.e., ethane, butane, *i*-butane, and *n*-butane, which could be formed over the precious metal catalysts, for example, Pt, Pd, Ru, and Rh. However, formation of these alkane species including CH_4 could be suppressed by using Cu catalyst. It should be noted that methanol was completely reformed for all cases studied here. It should be pointed out that the thermodynamically plausible products might not be produced experimentally. The products observed in the experiment strongly depended on the catalysts used.

3.6. Methanol steam reforming: coke-formed and coke-free regions

As generally known, coke formation during the catalytic steam reforming could lead to deactivation of catalysts, resulting in low durability and activity. Coke formation was considered in the thermodynamic calculation of SR of methanol in this section. We have determined the temperature region where coke presences or absences in the reforming products. Coke or coke

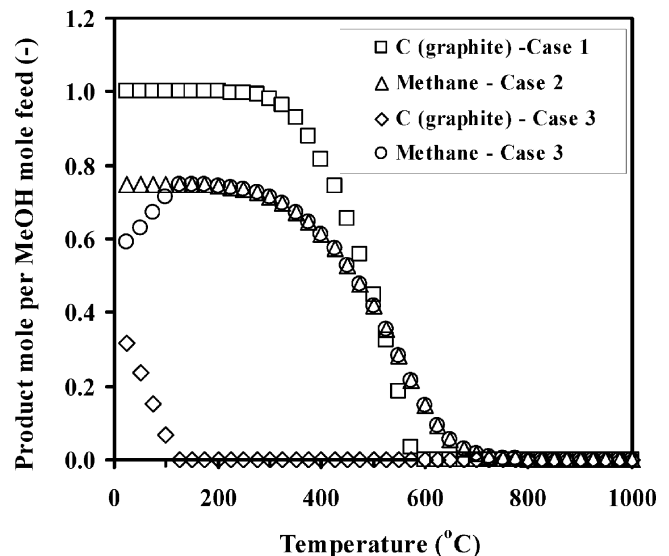


Fig. 8. Equilibrium plausible products thermodynamically produced from $MeOH$ SR as a function of temperature at S/C of 2 and pressure of 1 atm.

Table 1
Optimal operating conditions for MeOH SR: temperature, pressure and steam-to-MeOH ratio

Temperature (°C)	100–200	150–225	100–150	50
Pressure (atm)	1	1	1	1
S/C	1	1.5–2	2–3	4–5
MeOH conversion (%)	≥98.8	≥99.9	≥99.6	≥99.4
H ₂ yield (%)	96.4–97.0	98.7–99.8	99.5–99.8	99.0–99.4
H ₂ concentration (% on a dry basis)	74.3–74.4	74.8–75.0	74.9–75.0	74.8–74.9
CO concentration (% on a dry basis)	1.4–2.7	≤1	≤0.1	≤10 ppm

with methane was added into the thermodynamic compound basis sets. Methane was considered as the most abundant product produced during MeOH SR. Coke-formed and coke-free regions were thermodynamically determined as shown in Fig. 9. The temperature, at which the first disappearance of carbon T_c was achieved, was plotted as a function of S/C ratio. The regions above and below the lines are the coke-free and coke-formed regions, respectively. In the case coke was added to the basis set (Case 1), T_c decreased from ca. 800 to 400 °C, when the S/C ratio increased from 0.1 to 10. When methane was taken into account (Case 3), the T_c drastically decreased from ca. 800 to 175 °C with increasing S/C from 0.1 to 1.5. Further increase in S/C from 1.5 to 5 gradually decreased T_c from 175 to 25 °C. It was found that the T_c is in good agreement with that reported by Lwin et al. [26]. It should be noted that MeOH conversion was 100% for all operating condition in the case coke was thermodynamically favored in the reforming system.

3.7. Methanol steam reforming: optimal operating condition

The optimal operating condition of hydrogen production for fuel cell is discussed to obtain maximum hydrogen production and minimum carbon monoxide formation with complete conversion of fuel. Steam-to-carbon ratio, pressure, and temperature have to be optimized. With an optimal condition, high quality of reformed fuel for fuel cell could be achieved with efficient

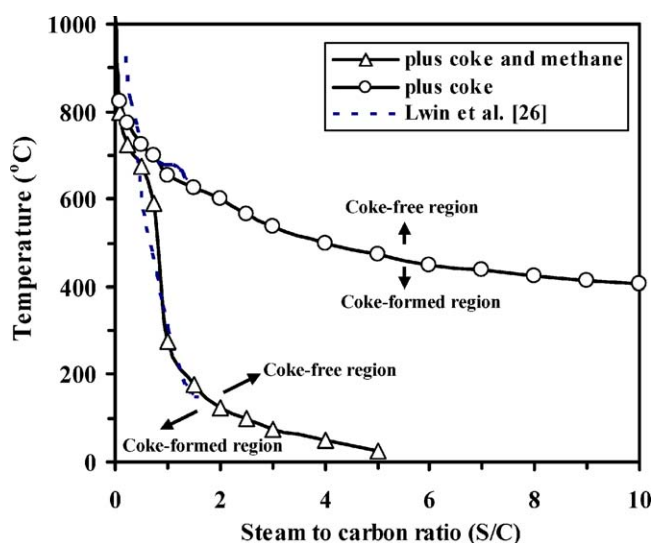


Fig. 9. Coke-formed and coke-free regions as a function of steam-to-carbon ratios (S/C) at pressure of 1 atm.

energy consumption and size of reactor. The difference in hydrogen and CO production calculated as a function of S/C and temperature at 1 atm was evaluated. The optimal region of the hydrogen–carbon monoxide difference was in the temperature range of 100–300 °C and $S/C \geq 1.5$ for MeOH SR.

On the basis of the equilibrium calculation with coke and hydrocarbon compounds excluded, several candidates for the optimal operating conditions which lead to large difference in H₂–CO production are listed in Table 1. The temperatures, pressure, and S/C ratios were chosen in the range of 100–225 °C, 1 atm, and 1–3, respectively. For stoichiometric ratio $S/C = 1$ and temperature = 100–200 °C, MeOH conversion ≥98.8% and hydrogen yield 96.4–97.0% were obtained with relatively high CO concentration 1.4–2.7%. An almost complete conversion (≥99.9%) and hydrogen yield (98.7–99.8%) with CO concentration (≤1%) could be achieved when the temperature and S/C were intentionally raised up to 150–225 °C and 1.5–2, respectively. Increasing S/C to 2–3 and decreasing temperature to 100–150 °C brought about the decrease in CO concentration to merely lower than 0.1%, while keeping high MeOH conversion and hydrogen yield. However, the higher steam-to-carbon ratio requests higher volume of the reactor because of higher steam volumetric flow, and consumed higher input heat duty because of higher vaporization energy. As for the limitation for PEFCs operation, CO level in reformed gas feed to the fuel cell is limited typically below 10 ppm. When the priority attention was paid for CO concentration, temperature and S/C ratio were optimized to $T_r = 50$ °C and $S/C = 4–5$. However, the equilibrium cannot be attained in this condition on existing catalysts.

The optimal operation condition was evaluated in the viewpoint of thermodynamics. The favorable condition for MeOH SR is to operate at temperature and steam over fuel ratio as low as possible. Operating at low temperature and S/C are advantageous for short start-up time and energy consumption. However, it should be pointed out that durability, activity, and selectivity of the catalyst along with side-reactions have to be considered from the practical point of view. Note that the thermodynamic study showed that the by-products such as coke and methane can be thermodynamically produced. Therefore, in case such by-products are selective over the reforming catalysts, the compound basis set for the calculation has to take the by-products into account.

4. Conclusions

Thermodynamic consideration for methanol steam reforming (MeOH SR) via Gibbs free minimization to evaluate the effect of

reforming temperature (25–1000 °C), pressure (0.5–3 atm), and plausible product species has been studied. The principal set of compounds involved in the calculation was methanol, water, hydrogen, carbon dioxide, and carbon monoxide. Based on the thermodynamic calculation, the conclusions were summarized in the following:

- MeOH SR provided hydrogen-rich feeds for fuel cell application. A complete MeOH conversion and hydrogen concentration exceeding 70% on a dry basis was obtained at S/C = 1 when the temperature was in the range of 200–500 °C at atmospheric pressure. The maximum concentration and yield of hydrogen could be achieved at almost 75% on a dry basis and 100%, respectively.
- On the basis of the reforming efficiency, the operating condition was optimized in the temperature range of 100–225 °C, S/C of 1.5–3, and pressure at 1 atm. The calculation showed that the requirement from sufficiently low CO concentration (<10 ppm) is too severe for the existing catalysts ($T_r = 50$ °C).
- At equilibrium, only methane and coke thermodynamically coexist with H₂O, H₂, CO, and CO₂, while C₂H₆, C₃H₈, *i*-C₄H₁₀, *n*-C₄H₁₀, CH₃OH, C₂H₅OH, C₃H₇OH, *i*-C₄H₉OH, *n*-C₄H₉OH, and DME were suppressed at essentially zero. The temperature for coke-free region decreased by increasing S/C ratio.
- At a given the temperatures higher than ca. 150 °C, varying pressures from 0.5 to 3 atm did not affect the MeOH conversion and hydrogen yield since MeOH conversion attained the maximum at 100%.

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