The Influences of the Physical Parameters on the Performance of a Methanol Steam Reformer

Yu-Jen Chiu*, Yu-Cheng Lin, Guo-Jhen Syu
Department of Mechanical Engineering
Taipei Chengshih University of Science and Technology
Taipei, Taiwan
*E-mail: yj chiu@tpcu.edu.tw

Abstract — Methanol is regarded as an important feedstock for hydrogen production due to its high energy density and superior transportability. In this work, an experimental platform was constructed to evaluate the performance of a small-scale methanol steam reformer. The objective was aimed at the influences of various physical parameters on the methanol steam reforming (MSR) process. The hydrogen, carbon monoxide and carbon dioxide production rate, as well as methanol conversion, were experimentally analyzed with respect to different levels of the space velocity of the feedstock, the porosity and temperature of the catalyst bed, and the steam-to-carbon (S/C) ratio. It revealed the methanol conversion was sensitive to the temperature of the catalyst bed and the catalyst loading. The maximum methanol conversion does not necessarily correspond to maximum hydrogen production rate since a portion of the generated hydrogen was extracted during the water-gas shift process. The hydrogen production rate can reach about 2.7 times of the methanol feed rate. In addition, the by-product concentration of CO was significantly influenced by temperature and S/C ratio. On the other hand, a packed-bed dispersion model of methanol conversion is established to analyze the influences of the aforementioned physical parameters. Accordingly, dimensionless parameter groups can be discussed as well. It is anticipated to provide clues to systematic design of a MSR reactor.

Keywords — methanol steam reforming (MSR), conversion, hydrogen production, dispersion model, packed-bed reactor

I. INTRODUCTION

Hydrogen energy is emission-free, portable and possesses high energy density. It is therefore considered one of the potential energy resources. In fuel cell applications, the electrical efficiency and the combined heat and power (CHP) efficiency derived from hydrogen can achieve 60% and 90%, respectively. Although hydrogen is abundantly reserved on earth, it should be extracted from a variety of hydrides. These include fossil fuels like natural gas and alcoholic fuels, as well as biomass and water with power input from renewable energy resources. In the near future, hydrogen produced from fossil energy, accompanying carbon-dioxide capture technologies, can still play a significant role in the progress of the emerging hydrogen economy.

Methanol steam reforming (MSR) is considered one of the potential processes to acquire hydrogen [1]. Although it has been a mature technology for large-scaled industrial applications, the issues on small-scaled and portable demand accompanying fuel cell applications are still open to be investigated. In addition to the catalyst recipes, a variety of physically parameters play significant roles in an MSR reactor [2]. For example, Jang et al. established a 3D numerical model for a small MSR reactor to predict the influences of the flow channel types, reactant flow rate, and reactor temperature on the methanol conversion [3]. Dusterwald et al. indicated the steam-to-carbon ratio ranging between 1.0 and 2.0 is preferable to an MSR process [4]. Dixon studied the particle size of the catalyst with respect to the diameter of the packed-bed reactor and concluded the ratio should be considered an important design parameter [5].

Since various chemical and physical parameters, as well as operating variables, affect the performance of an MSR reactor, researchers adopted dimensionless parameter groups to pursue systematic guidelines for MSR design. For instance, a quasimon-dimensional quantity, space velocity (SV, in s⁻¹), is considered an important index that correlates the operating variable (flow rate of the reactant) with the geometric parameter (reactor volume) [6, 7]. Erickson et al. defined characteristic time as the reciprocal of a first-order reaction constant. The index was then related to methanol conversion and the consistency of the relationship was verified by introducing different flow-field patterns, geometric parameters of the reactor, and the particle size of the catalyst [8, 9]. Wijaya et al. introduced the Damköhler number to connect with methanol conversion. The reaction rate (chemical aspect) and the convective mass transfer rate (physical aspect) were considered simultaneously meanwhile the rate law was fitted based on experimental results [10].

In this paper, an MSR testing platform was constructed. It is capable of adjusting molar flow rates of the feedstock (methanol and water), controlling and diagnosing the reactor temperature, and quantitatively analyzing the concentration of the produced gases. Experimental results that correspond to different temperature, S/C ratio, space velocity, and catalyst loading were presented. Furthermore, this work incorporates two dimensionless parameter groups: Bodenstein number and Damköhler number into a dispersion model to analyze the methanol conversion...
II. EXPERIMENT PLATFORM

Methanol steam reforming is best carried out over a copper based catalyst [11]:

\[ \text{CH}_3\text{OH} (g) + \text{H}_2\text{O} (g) \leftrightarrow 3\text{H}_2 + \text{CO} \quad \Delta h = +49.6 \text{ kJ mol}^{-1} \quad (1) \]

It is supposed carbon monoxide is first generated (methanol decomposition) and then reacts with water to form carbon dioxide (water-gas shift):

\[ \text{CH}_3\text{OH} (g) \leftrightarrow 2\text{H}_2 + \text{CO} \quad \Delta h = +90.8 \text{ kJ mol}^{-1} \quad (2) \]

\[ \text{CO} + \text{H}_2\text{O} (g) \leftrightarrow \text{H}_2 + \text{CO}_2 \quad \Delta h = -41.1 \text{ kJ mol}^{-1} \quad (3) \]

An MSR testing platform was therefore constructed in this work to analyze the concentration of the produced hydrogen, carbon monoxide, and carbon dioxide, as was shown in Fig. 1.

On the platform, liquid methanol and water were fed by precision pumps (Eyela MP-1000) into two tanks and then evaporated by boilers (NEWLAB MN-500C) individually. The temperatures of the gaseous methanol and steam were raised up to 383 K and 373 K, respectively. The delivery of the gaseous methanol and steam were regulated by two rotameters (in full scale of 2 L). The rotameters adopted were pre-calibrated by a precision mass flow controller (ALICAT MC-SSLPM). Before entering the MSR reactor, the gaseous methanol and steam were mixed and kept heating up to about 480 K. A cylindrical MSR catalyst bed was made by stainless steel with its diameter and length being 30 mm and 100 mm, respectively. The catalyst bed was also surrounded by electric heaters meanwhile the operating temperature was controlled via power supplies, temperature control modules, and thermocouple feedbacks. Copper based commercial catalyst (ALFA HiFUEL R120, CuO/ZnO/Al_2O_3) was employed in this work. The catalyst pellets were packed to achieve a porosity of 35%. The high temperature products out of the MSR reactor were delivered into a condenser, so that the unreacted methanol and water can be trapped in liquid phase while the gaseous products can be conducted into a gas chromatography (China Chromatography GC3000) and analyzed by a thermal conductivity detector (TCD). Moreover, the volumetric flow rate of the gaseous products were also measured by another rotameter (in full scale of 5 L) to derive the hydrogen production rate. There were totally 14 thermocouples installed within the flow pipes and the reactor meanwhile the corresponding temperatures were recorded by a DAQ interface (National Instruments NI 9172, NI 9211).

By adjusting the temperature of the MSR reactor and the molar flow rate of methanol and water, five levels of operating temperatures, S/C ratios, and space velocities were assigned for experiment, as were shown in Table 1.

<table>
<thead>
<tr>
<th>Set</th>
<th>Temperature (K)</th>
<th>S/C Ratio</th>
<th>Space Velocity (min^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>503, 523, 543, 563, 583</td>
<td>1.0</td>
<td>35</td>
</tr>
<tr>
<td>B</td>
<td>563</td>
<td>0.5, 1.0, 1.5, 2.0, 2.5</td>
<td>35</td>
</tr>
<tr>
<td>C</td>
<td>563</td>
<td>1.0</td>
<td>21, 28, 35, 42, 49</td>
</tr>
</tbody>
</table>

III. DISPERSION MODEL

The rate law of the MSR reaction (1) can be expressed in the form of [11]

\[ r_{st} = -k_0 \exp\left(\frac{-E_a}{RT}\right)P_M^m P_w^n \]  

where \( P_M \) and \( P_w \) denote the partial pressures of the feeding methanol and water, respectively. Purnama et al. fitted (4) experimentally to obtain \( m = 0.6 \) and \( n = 0.4 \) [12]. A one dimensional methanol concentration dispersion model of a cylindrical packed-bed reactor can be expressed as [6]:

\[ D_r \frac{d^2C_M}{dz^2} - \frac{dC_M}{dz} + r_{st} = 0 \]

where \( D_r \) and \( u \) represent the dispersion coefficient and the average volumetric flow rate, respectively. By normalizing the position coordinate \( Z = z/L \) and assuming ideal gas state equation \( P = C/RT \), (5) can be alternatively expressed as

\[ D_r \frac{d^2C_M}{dz^2} - \frac{dC_M}{dz} - \tau k C_M^{na} C_w^n = 0 \]  

where \( \tau = L/u \) is the residence time.

Moreover, the definition of methanol conversion is

\[ X_M = \frac{C_{M0} - C_M}{C_{M0}} \]

and the steam concentration regarding reaction (1) is

\[ C_w = C_{w0} \left[ \frac{1 - X_M}{1 + X_M} \right] \frac{P}{P_{ref}} \left( \frac{T_{ref}}{T} \right) \]

where \( C_{M0} \) and \( C_{w0} \) are the reference pressure and temperature, respectively. Accordingly, one can obtain

\[ \frac{D_r}{uL} \frac{d^2X_M}{dz^2} - \frac{dX_M}{dz} + \tau k \left( \frac{1 - X_M}{1 + X_M} \right)^n C_M^{m-1} C_w^n (\gamma - X_M)^\gamma = 0 \]  

where \( \gamma \) denote the methanol concentration and S/C ratio at the inlet of the MSR reactor, while \( P_{ref} \) and \( T_{ref} \) are reference pressure and temperature, respectively.
When assuming (1) as first order reaction \((m+n=1)\), the methanol concentration dispersion model is then
\[
d^2 X_M \frac{dX_M}{dZ} + \mu_L \frac{dX_M}{dZ} + \mu_L \cdot \tau k \cdot \frac{(1-X_M)^{m}(\gamma-X_M)^{n}}{(1+X_M)^{m+n}} = 0
\]
\[(10)\]

It is noted that the Bodenstein number is \(Bo = \frac{uL}{D}\), meanwhile the Damköhler number is \(Da = \tau k\) for a first order reaction. A dimensionless dispersion model is then achieved. Finally, (10) can be solved accompanying Danckwerts boundary conditions \([6, 7]\):

At \(Z = 0\):
\[
\left. \frac{dX_M}{dZ} \right|_{Z=0} = -X_M(0^+) = 0
\]
\[(11)\]

At \(Z = 1\):
\[
\frac{dX_M}{dZ} = 0
\]
\[(12)\]

Equations (10)-(12) were coded and solved by Matlab® programs in this work.

IV. RESULTS AND DISCUSSIONS

A. Experimental Results

Based on experiment set A, the temperature effects on the concentration and the production rate of the produced gases were shown in Fig. 2. It indicates temperature has little influence on the mole fraction and the production rate of hydrogen when the temperature is raised from 503 K to 583 K. In our experiment, the mole fraction of hydrogen remained around 0.71 meanwhile the production rates were about 93 mmol min\(^{-1}\). On the other hand, the temperature effects on CO and \(\text{CO}_2\) are more evident. Both the mole fraction and the production rate of CO revealed an increase tendency progressively when the temperature was raised. On the contrary, the mole fraction and the production rate of \(\text{CO}_2\) were suppressed. The results meet the description of the reactions (2) and (3). Since the former (the first stage reaction) is an endothermic reaction, an increase in temperature benefits the production of CO. Nonetheless, (3) is an exothermic reaction (the second stage reaction) and the \(\text{CO}_2\) formation can be confined at a higher temperature. It is also noted the sum of the produced CO and \(\text{CO}_2\) was kept at a rate around 37 mmol min\(^{-1}\).

Fig. 3 shows the results of experiment set B. The space velocity of the steam-methanol mixture delivered in to the MSR reactor was kept at 35 min\(^{-1}\). The molar ratio of steam to methanol (S/C ratio) was ranging from 0.5 to 2.5. It is observed that the molar fraction of hydrogen slightly increased from 0.68 to 0.72, while the production rate declined significantly when the portion of the methanol in the feedstock was reduced since (2) is the critical reaction in an MSR process. Moreover, both the mole fraction and the production rate of CO diminished when the portion of the steam in the feedstock was increased. It is because sufficient steam is beneficial for the reaction (2) to transform CO into \(\text{CO}_2\). It is also observed that the effect of S/C ratio on the production rate of \(\text{CO}_2\) was insignificant.

In experiment set C, the temperature and the S/C ratio were kept at 583 K and 1.0, respectively. It is observed from Fig. 4 that the volumetric flow rate, or alternatively the space velocity, of the feedstock had little influence on the
concentration of the generated gases regarding the experiment conditions. In addition, the production rates of the generated gases were approximately proportional to the space velocity.

The temperature effect on the methanol conversion was depicted in Fig. 5. According to the results of experiment set A, the methanol conversion increased accompanying an increase in temperature, and then tended to approach an ultimate value, i.e. 92%. By inserting a number of stainless steel meshes into the reactor, the catalyst was equally supported and packed to achieve a porosity of 60%. The experiment set A was performed in this lower catalyst loading. The methanol conversion was therefore reduced more significantly, as was shown in Fig. 5. However, the methanol conversion eventually reached the similar value of 92%. Based on the experiment set B, the influence of S/C ratio on the methanol conversion was shown in Fig. 6(a). It seems to be the minor factor when comparing with the temperature effect, although the methanol conversion slightly enhanced when the S/C ratio was increased. The ratios of the hydrogen production rate to the steam supply rate (H/S ratio) and to the methanol supply rate (H/C ratio) were depicted in Fig. 6(b). It is observed that the H/S ratio significantly declined when the S/C increased, while the H/C ratio gradually increased from 2.1 to 2.7. The results met the reasonable stoichiometric ratio in (2) at lower S/C ratio, and then enhanced due to the reaction (3) to approach the overall stoichiometric hydrogen to methanol ratio in the MSR reaction (1), i.e. 3.

B. Model Analysis

By solving the dispersion model depicted in (10)-(12), the preliminary analysis on the methanol conversion was shown in Fig. 7. In Fig. 7(a), \( k_0 = 4 \times 10^6 \) (mol s\(^{-1}\) g\(_{cat}\) bar\(^{-1}\)), \( E_a = 76 \) (kJ mol\(^{-1}\)), \( \gamma = 1 \), \( D_e = 50 \) (cm\(^2\) s\(^{-1}\)), the porosity of the catalyst bed \( \varepsilon_1 = 35\% \), and the conditions of experiment set A listed in Table. 1 were introduced. The distribution of methanol conversion within the MSR reactor was illustrated in Fig. 7(a). At the outlet of the reactor, the relationship between temperature and methanol conversion was shown in Fig. 7(b). When the porosity of the catalyst bed was alternatively set to be \( \varepsilon_2 = 60\% \), the variation of the methanol conversion due to temperature change was also depicted. The tendency of the curves was consistent with the experiment results shown in Fig. 5. It verified the feasibility of the proposed dispersion model to analyze the performance of a MSR reactor. Further tasks of the experimental data fitting and model investigation are in progress.

V. CONCLUSIONS

An MSR testing platform was constructed in this work. The influences of temperature, S/C ratio, space velocity, and catalyst loading on the performance of a MSR reactor were experimentally evaluated and analyzed. In the present paper, the temperature and the S/C ratio were suggested to be more significant for an MSR process based on the illustrated conditions. Furthermore, a dispersion model of methanol conversion was proposed in a dimensionless form. Its feasibility to analyze the performance of a MSR reactor was preliminarily verified by referring to experimental results. Further tasks regarding the experimental data fitting and model investigation are in progress.

ACKNOWLEDGMENT

This work was financially supported by Ministry of Science and Technology, Taiwan, R.O.C. (MOST 103-2221-E-149-006)
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