Production of synthetic alcohol from syngas using MoS$_2$/γ-Al$_2$O$_3$

S. W. Chiang, C. C. Chang, H. Y. Chang, C. Y. Chang*

Graduate Institute of Environmental Engineering, Nation Taiwan University, Taipei 106, Taiwan
* Corresponding Author. Tel: (886) 223638994, Fax: (886) 223638994, E-mail: cychang3@ntu.edu.tw

Abstract: This study examined the transformation of the biomass gasification synthesis gas (syngas, CO and H$_2$) to liquid fuels and chemicals via the high pressure fixed packed bed (HPFPB). The MoS$_2$/γ-Al$_2$O$_3$ catalyst was packed in the packed bed (PB) to enhance the selectivity (S) and yield (Y) products. The effect of reaction temperature (T), pressure (P$_{ST}$), gas flow rate (Q$_G$) and H$_2$/CO (vol./vol.) ratio on the system performance were investigated. Typical reaction conditions unless otherwise specified were as follows: T = 423, 473, 523 and 573 K, P$_{ST}$ = 3 MPa, Q$_G$ = 300 cm$^3$ min$^{-1}$, and mass of catalyst (m$_S$) = 30 g.

The main products include CH$_4$, C$_2$H$_6$ and C$_2$H$_5$OH (EtOH) that EtOH being the target product. The results indicate that with packing MoS$_2$/γ-Al$_2$O$_3$ catalyst in PB, the conversion of CO (X$_{CO}$) and alcohol production rate (R) are highly dependent on T. At T = 573 K, X$_{CO}$ = 8.19%, R of CH$_4$ (R$_{CH4}$) = 194.1 mg h$^{-1}$ and selectivity of CH$_4$ (S$_{CH4}$) = 34.57%. For the production rate of C$_2$H$_5$OH (R$_{EtOH}$), the maximum R$_{EtOH}$ of 134.25 mg h$^{-1}$ takes place at T = 523 K while X$_{CO}$ = 8.10% and S$_{EtOH}$ = 51.98%. As T increase to 573 K, the EtOH is further decomposed into simple hydrocarbons (HCs) such as C1-C3 alkanes. Thus, for producing more alcohols and less alkanes, the optimal temperature condition is 523 K. For the case of varying H$_2$/CO ratio, the values of X$_{CO}$ are about 7.55 to 8.32%) at 523 K with H$_2$/CO ratios of 1 to 4, indicating no significant variation. However, the optimal ratio of H$_2$ to CO to produce EtOH is 2 with maximum R$_{EtOH}$ = 134.25 mg h$^{-1}$ and S$_{EtOH}$ = 51.98% while X$_{CO}$ = 8.10%, R$_{CH4}$ = 56.05 mg h$^{-1}$ and S$_{CH4}$ = 10.85%. Hence, increasing the H$_2$/CO ratio to 3 or 4 is not beneficial for the formation of EtOH. The results also show that a higher PST of HPFPB yields more products. For the EtOH production, the maximum R$_{EtOH}$ (= 156.65 mg h$^{-1}$) occurs at P$_{ST}$ = 3.6 MPa with corresponding S$_{EtOH}$ = 51.16%, X$_{CO}$ = 9.57%, R$_{CH4}$ = 70.31 mg h$^{-1}$ and S$_{CH4}$ = 12.46%. Among various Q$_G$ of 300, 450, 600 to 900 mL min$^{-1}$ of HPFPB tested, the best X$_{CO}$ is at Q$_G$ = 300 mL min$^{-1}$ with X$_{CO}$ = 8.10%, R$_{CH4}$ = 56.05 mg h$^{-1}$ and S$_{CH4}$ = 10.85%. Also, the maximum Y$_{EtOH}$ take place at Q$_G$ = 300 mL min$^{-1}$ with corresponding S$_{EtOH}$ = 51.98%. It shows that a low flow rate gives a longer residence time for reaction of the syngas and thus enhances the yield of products. However, there’s no advance for S$_{EtOH}$.

For the production of EtOH from syngas, the Y$_{EtOH}$, S$_{EtOH}$ and R$_{EtOH}$ are key factors for the success of process. The results of this study shows that MoS$_2$/γ-Al$_2$O$_3$ catalyst can give satisfactory S$_{EtOH}$ and R$_{EtOH}$, especially the Y$_{EtOH}$ high selectivity.

Keywords: Reforming of syngas; Synthesis of alcohol; MoS$_2$/Al$_2$O$_3$; catalytic synthesis; alcohol; alkane

1. Introduction

Energy crisis has been a great concerned issue in recent years. With the continued climbing of crude oil price, studies on alternative energy become more and more essential. The use of biomass, such as agriculture residues and woody waste, to provide energy and chemicals is receiving increasing interest because these resources can supplement the existing supplies of raw materials while have less net environmental impact [1]. The biomass of agriculture and the biomass fibers of municipal solid waste (MSW) are among the suitable bio-energy sources that can be used for generation energy [1-2].

Gasification technologies have been developed for the possible replacement of traditional combustion technologies because of their higher power generation efficiency while lower environmental pollution [2]. Gasification is a thermochemical process yielding major product of synthesis gas (syngas) consisting of CO and H$_2$. Syngas can be used to produce hydrocarbons such as ethanol (EtOH) via Mo-based catalytic reaction and other high-value-added fuels via the Fischer-Tropsch process. Although the syngas has been also used as fuel gas, however, its storage, stabilization and transportation exhibit some problems. On the other
hand, alcohols converted from syngas have high heating value with small volume and are
stable as liquid phase. Moreover, the use of EtOH as a part of the automobile fuel offers the
same chemical energy as that of gasoline. Besides, ethanol is a good additive for improving
gasoline octane value and burning efficiency [3].

In this study, a high pressure fixed packed bed (HPFPB) with continuous flow was used to
synthesize the syngas yielding alcohols. A MoS2/γ-Al2O3 catalyst was packed in the bed to
enhance the production. The MoS2 based catalysts, such as K2CO3/MoS2 and Ni-
K2CO3/MoS2, have been already verified as effective catalysts in the synthesis of mixed
alcohols [4-7]. The distinct points of this study were the use of HPFPB and preparation
method of MoS2 on the γ-Al2O3 support with high surface of catalyst. The production rates
(R), yield (Y) and selectivity (S) of alcohols and conversion of CO (XCO) were examined and
elucidated.

2 Materials and Methods

2.1 Preparation of MoS2/γ-Al2O3

The MoS2 was loaded on γ-Al2O3 pellet (MoS2/γ-Al2O3). In preparation, about 30 g
γ-Al2O3 (φ = 3 mm) were soaked in 200 mL solution containing 5% ammonium
heptamolybdate ((NH4)6Mo7O24) with the adjustment of pH < 2 using nitric acid for
adsorbing ionic Mo on the alumina surface for 12 h. It was then sintered at 773 K with N2 for
3 h to form MoXOY/γ-Al2O3. The resulted MoXOY/γ-Al2O3 was further reduced and
sulfurized in the mixed gas stream of H2S/H2 with volume ratio of 5/95 at 673 K for 2 h to
produce MoS2/γ-Al2O3 catalyst [8]. The γ-Al2O3, MoS2 and (NH4)6Mo7O24 were supplied
by First Chemical (Taipei, Taiwan), ProChem (Miaoli, Taiwan) and J.T. Baker (Phillipsburg,
New Jersey, USA), respectively.

2.2 HPFPB system

The HPFPB system (Fig. 1) was carried out via continuous flow type operation. The
synthesis reaction proceeded in a high pressure. Two packing materials of MoS2/γ-Al2O3 and
spherical glass beads were used and tested in the packed bed. The polar organic products such
as alcohols and acids were collected by DI water (4 °C) in a condenser. The syngas was
simulated with H2/CO mole ratio of 2. The HPFPB system was operated under the conditions
with mass flow rates of H2 and CO (dmH2/dt and dmCO/dt) of 1070.4 and 7492.8 mg h−1, gas
flow rate of syngas (QG) = 300 mL min−1, temperature (T) = 423-573 K, mass of catalyst (mS)
= 30 g, flow rate (QG) = 300-900 mL min−1, gas hourly space velocity (GHSV) = 600-1800
cm3 gcat−1 h−1, and pressure (PST) = 1.5-3.6 Mpa (reading at 298 K).

2.3 Products analysis

The analyses of gaseous organic compounds were performed using the gas
chromatography/flame ionization detector (GC/FID, 6890 GC, Agilent Technologies, Santa
Clara, CA, USA) with AB-5 column (30m × 0.53mm × 5.00 μm, Abel Industries, Pitt
Meadows, BC, Canada) to separate the organic products. A purge-and-trap sample
concentrator (Model 4560, OI Analytical, College Station, TX, USA) was used to purify and
inject liquid samples into GC/FID for analyses.
3 Results and discussion

3.1 Properties of catalyst and support

The MoS$_2$/Al$_2$O$_3$ catalyst used is spherical with 3 mm diameter and bulk density of 3.2055 g cm$^{-3}$. The MoS$_2$ was loaded on the surface of porous Al$_2$O$_3$ pellet. The BJH (Barrett-Joyner-Halenda) average pore sizes obtained by adsorption and desorption are 70.404 and 57.841 Å, respectively, indicating mesoporous nature of catalyst. The corresponding BET surface area is 210.345 m$^2$ g$^{-1}$. The XRD (X-ray diffraction) spectrum of catalyst surface is shown in Fig. 2, exhibiting significant specific characteristics of MoS$_2$ at $2\theta = 14.5^\circ$, 39.6$^\circ$ and 60.18$^\circ$. 

![Diagram](image1)

Fig. 1. Schematic diagram of HPFPB system.

![Diagram](image2)

Fig. 2. XRD spectrum of MoS$_2$/Al$_2$O$_3$. 

---

539
3.2 Effect of temperature

As shown in Fig. 3a, the production rate $R$ of alkane via $\text{MoS}_2/\gamma-\text{Al}_2\text{O}_3$ synthesis increases with increasing reaction temperature, especially when $T$ reaches 573 K. For the (b) alcohol products, the productions were not effected as the regular pattern as the increase $T$ for the alkane products.

![Fig. 3. Production rates of (a) alkane and (b) alcohol products at various temperatures via HPCPB-MoS$_2$ process.](image)

Table 1 illustrates the conversion of CO ($X_{\text{CO}}$) and selectivities (S) of synthesis products at the four different temperature conditions. Setting the reaction at the conditions of $T = 473$ K, $P_{\text{ST}} = 3 \text{ MPa}$, $H_2/\text{CO} = 2$, $Q_G = 300 \text{ cm}^3 \text{ min}^{-1}$, and $\text{GHSV} = 600 \text{ cm}^3 \text{ gcat}^{-1} \text{ h}^{-1}$, the selectivities of synthesis products shows the highest forming favourable $S_{\text{EtOH}} = 54.02\%$ within four different temperatures and accompanies with lower forming $S_{\text{CH}_4} = 2.09\%$. Since $X_{\text{CO}}$ is also a meaningful efficiency index, the best $X_{\text{CO}}$ is 8.19% while the condition at $T = 573$ K.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Conversion (%)</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>C$<em>4$H$</em>{10}$</th>
<th>CH$_3$CHO</th>
<th>MeOH</th>
<th>EtOH</th>
<th>PrOH</th>
<th>BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>423</td>
<td>0.59</td>
<td>1.19</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
<td>31.12</td>
<td>16.69</td>
<td>36.43</td>
<td>6.53</td>
<td>7.30</td>
</tr>
<tr>
<td>473</td>
<td>2.09</td>
<td>6.88</td>
<td>8.06</td>
<td>-</td>
<td>-</td>
<td>22.50</td>
<td>6.38</td>
<td>54.02</td>
<td>0.30</td>
<td>1.86</td>
</tr>
<tr>
<td>523</td>
<td>8.10</td>
<td>10.85</td>
<td>12.84</td>
<td>3.00</td>
<td>-</td>
<td>7.48</td>
<td>11.29</td>
<td>51.98</td>
<td>2.27</td>
<td>0.29</td>
</tr>
<tr>
<td>573</td>
<td>8.19</td>
<td>34.57</td>
<td>14.06</td>
<td>9.58</td>
<td>0.48</td>
<td>6.28</td>
<td>6.21</td>
<td>28.28</td>
<td>0.39</td>
<td>0.16</td>
</tr>
</tbody>
</table>

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

At first appearance, the highest $S_{\text{EtOH}}$ and the best $X_{\text{CO}}$ seem to be well performances. In fact, they still could not represent the optimal condition because of theirs uncompleted well-performances which comparing these with the condition at $T = 523$ K. Setting the reaction $T$ at 523 K is the optimal set point which not only yields more alcohol products, especially for higher $S_{\text{EtOH}}$, but also restrains the amount of alkanes formed.
3.3 Effect of H₂/CO ratio

Besides the temperature factor, the H₂/CO feed ratio is also a key adjustable variable affecting the conversion of syngas to ethanol or higher alcohols. The H₂/CO could be adjust to maximize S_{EtOH} and restrain methane forming that because methane is the most thermodynamically favored product, however, its economical value is less than alcohols [9]. The reactions of ethanol and methane are as the showing in following equations:

\[
\begin{align*}
2\text{CO} + 4\text{H}_2 & \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \quad \text{(1)} \\
\Delta H_r &= -61.20 \text{ kcal/mol; } \Delta G_r = -29.32 \text{ Kcal/mol} \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{(2)} \\
\Delta H_r &= -49.27 \text{ kcal/mol; } \Delta G_r = -33.97 \text{ Kcal/mol}
\end{align*}
\]

According the ratio of H₂/CO from the above equations, it is obvious to understand that higher ratio (eq. 2) is more favourable to produce methane than producing ethanol (eq. 1). As the shown in fig. 4, the productions present desired results which are higher production of alcohols accompany with lower production of alkanes when setting H₂/CO ratio as 2.

![Fig. 4. Production rates of (a) alkane and (b) alcohol products at various H₂/CO ratios via HPCPB-MoS₂ process. ◇, □, △, ○: C₁, C₂, C₃, C₄.](image)

Table 2. Conversion of CO and selectivities of products at various H₂/CO ratios.

<table>
<thead>
<tr>
<th>H₂/C O Conversion (%)</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₄H₁₀</th>
<th>CH₃CHO</th>
<th>MeOH</th>
<th>EtOH</th>
<th>PrOH</th>
<th>BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.55</td>
<td>11.84</td>
<td>15.01</td>
<td>11.21</td>
<td>-</td>
<td>5.09</td>
<td>8.97</td>
<td>44.9</td>
<td>1.82</td>
</tr>
<tr>
<td>2</td>
<td>8.10</td>
<td>10.85</td>
<td>12.84</td>
<td>3.00</td>
<td>-</td>
<td>7.48</td>
<td>11.29</td>
<td>51.98</td>
<td>2.27</td>
</tr>
<tr>
<td>3</td>
<td>8.01</td>
<td>12.67</td>
<td>12.34</td>
<td>3.94</td>
<td>-</td>
<td>6.97</td>
<td>12.69</td>
<td>48.73</td>
<td>2.13</td>
</tr>
</tbody>
</table>
Table 2 illustrates $X_{CO}$ and $S$ of synthesis products at the four different H$_2$/CO ratios. Setting the reaction at the conditions of $T = 523$ K, $P_{ST} = 3$ MPa, $Q_G = 300$ cm$^3$ min$^{-1}$, and GHSV = 600 cm$^3$ gcat$^{-1}$ h$^{-1}$, $X_{CO}$ is 8.10% and $S_{\text{EtOH}}$ and $S_{\text{CH}_4}$ are 51.89% and 10.85%, respectively. In these conditions, MoS$_2$ catalyst shows obvious favour for EtOH and slight restraint for CH$_4$. For this reason, the results of the shown at H$_2$/CO = 2 are desired and acceptable even if the conversion of CO is not the highest performance.

### 3.4 Effects of pressure

Increasing pressure is equal to increase the providing raw materials and the equilibrium concentration of products from the hydrogenation of CO [1]. As the shown in fig. 5, both of the productions of alkane and alcohol products increase as the increasing reaction pressure. Therefore, the effects of reaction pressure appear as though Le Chatelier's Principle.

![Production rates of (a) alkane and (b) alcohol products at various pressures via HPCPB-MoS$_2$ process.](image)

<table>
<thead>
<tr>
<th>$P_{ST}$ (MPa)</th>
<th>Conversion (%)</th>
<th>MeOH</th>
<th>EtOH</th>
<th>PrOH</th>
<th>BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>4.6</td>
<td>11.84</td>
<td>15.01</td>
<td>11.21</td>
<td>-</td>
</tr>
<tr>
<td>2.4</td>
<td>6.48</td>
<td>12.05</td>
<td>14.04</td>
<td>3.08</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>8.10</td>
<td>10.85</td>
<td>12.84</td>
<td>3.00</td>
<td>-</td>
</tr>
<tr>
<td>3.6</td>
<td>9.57</td>
<td>12.46</td>
<td>12.63</td>
<td>2.96</td>
<td>-</td>
</tr>
</tbody>
</table>

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

![Table 3. Conversion of CO and selectivities of products at various pressures.](image)
Table 3 illustrates $X_{\text{CO}}$ and $S$ of synthesis products at the four different reaction pressures (reading at 298 K). Setting the reaction at the conditions of $T = 523 \, \text{K}$, $\text{H}_2/\text{CO} = 2$, $Q_G = 300 \, \text{cm}^3 \, \text{min}^{-1}$, and $\text{GHSV} = 600 \, \text{cm}^3 \, \text{gcat}^{-1} \, \text{h}^{-1}$. As the increased pressure in this study, there are only increasing effects for $X_{\text{CO}}$ as the shown in table 3, however, the selectivities of both alkane and alcohol products are not affected by changing the reaction pressures.

### 3.5 Effects of flow rate

A high flow rate into the reactor gives a higher space velocity through the fixed catalytic bed, which is equivalent to change the volume of catalyst in the reactor. As the shown in fig. 6, increasing the flow rate also means more reactants input, enhancing the production rates for both of alkanes and alcohols.

![Production rates](image)

Table 4 illustrates the conversion of CO and selectivities of synthesis products at the four different flow rates. Setting the reaction at the conditions of $T = 523 \, \text{K}$, $\text{H}_2/\text{CO} = 2$, $P_{\text{ST}} = 3 \, \text{MPa}$, and $\text{GHSV} = 300 \, \text{cm}^3 \, \text{min}^{-1}$. As the shown in table 4, increasing the flow rate obviously decrease $X_{\text{CO}}$ because the retention time is too small to finish more number of completed reactions. The increase of space velocity results in a slight decrease in selectivity of alkanes while an insignificant increase of alcohols in the reaction products. Besides, the effects of changing flow rate are similar with those of the changing of reaction pressures.

### Table 4. Conversion of CO and selectivities of products at various flow rates.

<table>
<thead>
<tr>
<th>$Q_G$ (mL min$^{-1}$)</th>
<th>Conversion (%)</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>C$<em>4$H$</em>{10}$</th>
<th>CH$_3$CHO</th>
<th>MeOH</th>
<th>EtOH</th>
<th>PrOH</th>
<th>BuOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>8.10</td>
<td>10.85</td>
<td>12.84</td>
<td>3.00</td>
<td>-</td>
<td>7.48</td>
<td>11.29</td>
<td>51.98</td>
<td>2.27</td>
<td>0.29</td>
</tr>
<tr>
<td>450</td>
<td>5.44</td>
<td>10.54</td>
<td>12.95</td>
<td>2.52</td>
<td>-</td>
<td>7.54</td>
<td>10.91</td>
<td>52.91</td>
<td>2.37</td>
<td>0.26</td>
</tr>
<tr>
<td>600</td>
<td>4.83</td>
<td>10.41</td>
<td>12.18</td>
<td>2.70</td>
<td>-</td>
<td>7.82</td>
<td>11.16</td>
<td>53.14</td>
<td>2.34</td>
<td>0.25</td>
</tr>
<tr>
<td>900</td>
<td>4.12</td>
<td>10.25</td>
<td>12.14</td>
<td>2.68</td>
<td>-</td>
<td>8.38</td>
<td>11.39</td>
<td>52.50</td>
<td>2.40</td>
<td>0.26</td>
</tr>
</tbody>
</table>
4. Conclusions

In HPFPB system, the main organic products of alkane and alcohols of MoS$_2$/γ-Al$_2$O$_3$ catalytic synthesis are ethanol and methane, respectively. From the previous results shown, ethanol selectivity decreases at all temperatures when methane is the major product. For this reason, setting the reaction temperature at $T = 523$ K is the optimal set point which not only yields more alcohol products, especially for higher $S_{\text{EtOH}}$, but also restrains the amount of alkanes formed. Furthermore, it could increase $S_{\text{EtOH}}$ versus CH$_4$ while setting the H$_2$/CO feed ratio as 2. Considering the effects of $P_{\text{ST}}$ and $Q_{\text{G}}$, there are similar trends for both of alkane and alcohol products besides of the trend for the conversion of CO. Increasing the flow rate would decrease $X_{\text{CO}}$ because the retention time is too small to finish more number of completed reactions.

Taken together, these observations suggest that setting the parameter as $T = 523$ K, H$_2$/CO = 2, higher pressure, and lower flow rate to reach the purpose of obtaining higher $X_{\text{CO}}$ and outstanding $S_{\text{EtOH}}$.

References


