



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  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  catalyst was packed in the bed to enhance the production. The  $\text{MoS}_2$  based catalysts, such as  $\text{K}_2\text{CO}_3/\text{MoS}_2$  and  $\text{Ni-K}_2\text{CO}_3/\text{MoS}_2$ , 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  $\text{MoS}_2$  on the  $\gamma\text{-Al}_2\text{O}_3$  support with high surface of catalyst. The production rates (R), yield (Y) and selectivity (S) of alcohols and conversion of CO ( $X_{\text{CO}}$ ) were examined and elucidated.

## 2 Materials and Methods

### 2.1 Preparation of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$

The  $\text{MoS}_2$  was loaded on  $\gamma\text{-Al}_2\text{O}_3$  pellet ( $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ ). In preparation, about 30 g  $\gamma\text{-Al}_2\text{O}_3$  ( $\phi = 3 \text{ mm}$ ) were soaked in 200 mL solution containing 5% ammonium heptamolybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ) with the adjustment of  $\text{pH} < 2$  using nitric acid for adsorbing ionic Mo on the alumina surface for 12 h. It was then sintered at 773 K with  $\text{N}_2$  for 3 h to form  $\text{Mo}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ . The resulted  $\text{Mo}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$  was further reduced and sulfurized in the mixed gas stream of  $\text{H}_2\text{S}/\text{H}_2$  with volume ratio of 5/95 at 673 K for 2 h to produce  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  catalyst [8]. The  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{MoS}_2$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  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  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  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  $\text{H}_2/\text{CO}$  mole ratio of 2. The HPFPB system was operated under the conditions with mass flow rates of  $\text{H}_2$  and  $\text{CO}$  ( $\text{dmH}_2/\text{dt}$  and  $\text{dmCO}/\text{dt}$ ) of 1070.4 and 7492.8  $\text{mg h}^{-1}$ , gas flow rate of syngas ( $Q_G$ ) = 300  $\text{mL min}^{-1}$ , temperature ( $T$ ) = 423-573 K, mass of catalyst ( $m_S$ ) = 30 g, flow rate ( $Q_G$ ) = 300-900  $\text{mL min}^{-1}$ , gas hourly space velocity (GHSV) = 600-1800  $\text{cm}^3 \text{gcat}^{-1} \text{h}^{-1}$ , and pressure ( $P_{\text{ST}}$ ) = 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  $\times$  0.53mm  $\times$  5.00  $\mu\text{m}$ , 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.

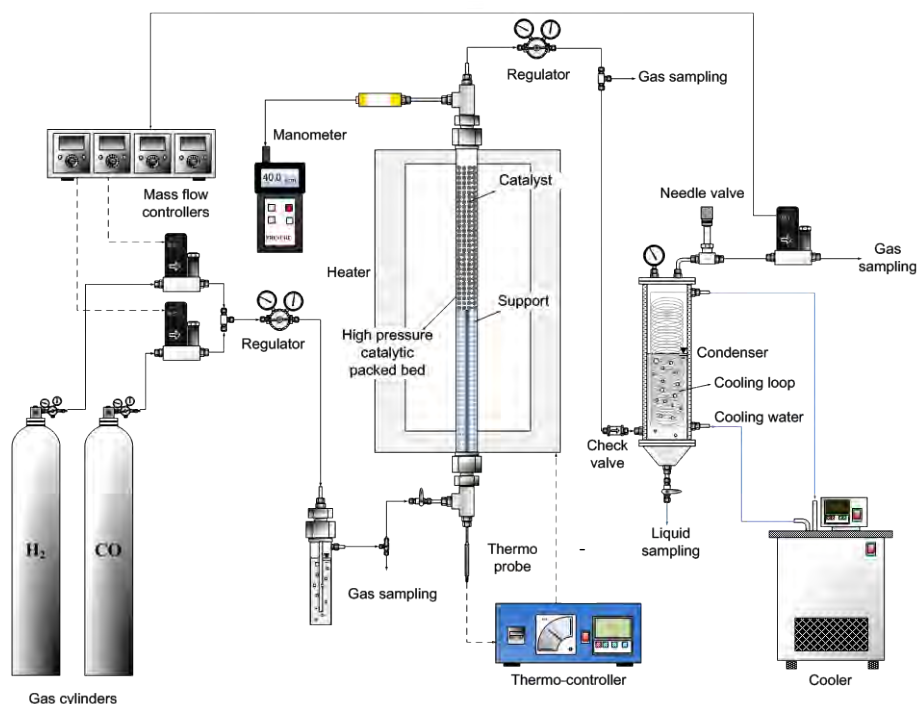


Fig. 1. Schematic diagram of HPFPB system.

### 3 Results and discussion

#### 3.1 Properties of catalyst and support

The  $\text{MoS}_2/\text{Al}_2\text{O}_3$  catalyst used is spherical with 3 mm diameter and bulk density of  $3.2055 \text{ g cm}^{-3}$ . The  $\text{MoS}_2$  was loaded on the surface of porous  $\text{Al}_2\text{O}_3$  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  $210.345 \text{ m}^2 \text{ g}^{-1}$ . The XRD (X-ray diffraction) spectrum of catalyst surface is shown in Fig. 2, exhibiting significant specific characteristics of  $\text{MoS}_2$  at  $2\theta = 14.5^\circ$ ,  $39.6^\circ$  and  $60.18^\circ$ .

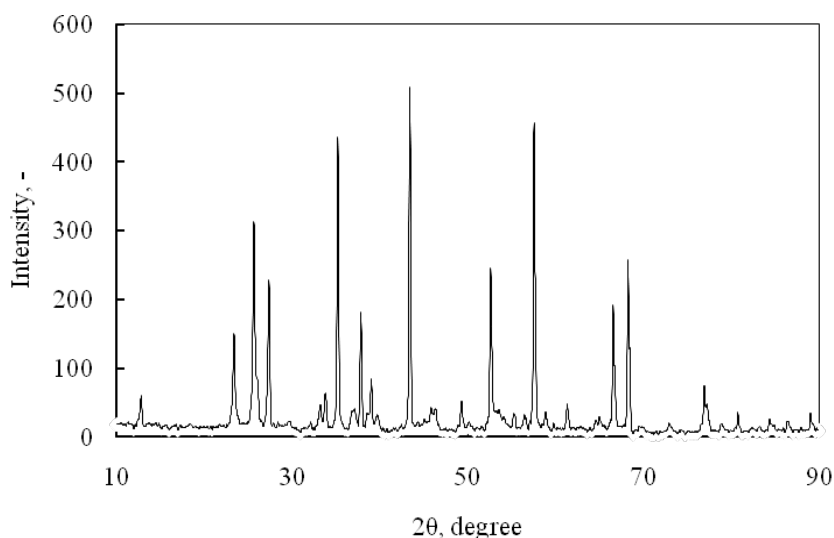


Fig. 2. XRD spectrum of  $\text{MoS}_2/\text{Al}_2\text{O}_3$ .

### 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.

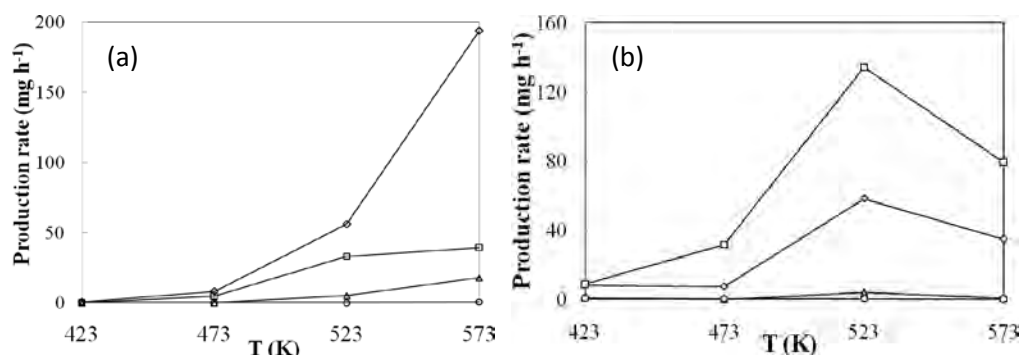


Fig. 3. Production rates of (a) alkane and (b) alcohol products at various temperatures via HPCPB- $\text{MoS}_2$  process.  $\diamond$ ,  $\square$ ,  $\triangle$ ,  $\circ$ : C1, C2, C3, C4.

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,  $P_{\text{ST}} = 3$  MPa,  $\text{H}_2/\text{CO} = 2$ ,  $Q_G = 300$   $\text{cm}^3 \text{min}^{-1}$ , and  $\text{GHSV} = 600$   $\text{cm}^3 \text{gcat}^{-1} \text{h}^{-1}$ , 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 1. Conversion of CO and selectivities of products at various temperatures.

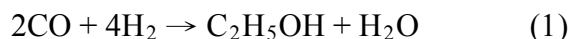
T (K)	Conversion (%)	Selectivity (%)								
		$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$	$\text{CH}_3\text{CHO}$	MeOH	EtOH	PrOH	BuOH
423	0.59	1.19	0.74	-	-	31.12	16.69	36.43	6.53	7.30
473	2.09	6.88	8.06	-	-	22.50	6.38	54.02	0.30	1.86
523	8.10	10.85	12.84	3.00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

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 their 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 H<sub>2</sub>/CO ratio

Besides the temperature factor, the H<sub>2</sub>/CO feed ratio is also a key adjustable variable affecting the conversion of syngas to ethanol or higher alcohols. The H<sub>2</sub>/CO could be adjust to maximize S<sub>EtOH</sub> 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:



$$\Delta H_r = -61.20 \text{ kcal/mol}; \Delta G_r = -29.32 \text{ Kcal/mol}$$



$$\Delta H_r = -49.27 \text{ kcal/mol}; \Delta G_r = -33.97 \text{ Kcal/mol}$$

According the ratio of H<sub>2</sub>/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 H<sub>2</sub>/CO ratio as 2.

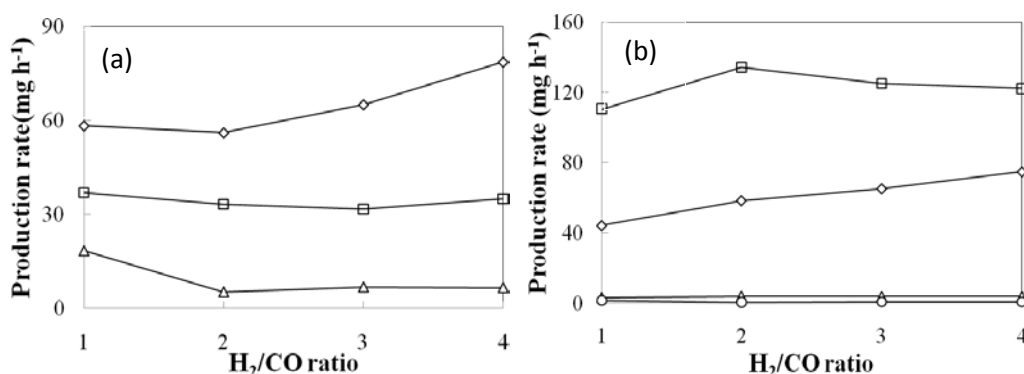


Fig. 4. Production rates of (a) alkane and (b) alcohol products at various H<sub>2</sub>/CO ratios via HPCPB-MoS<sub>2</sub> process. ◇, □, △, ○: C1, C2, C3, C4.

Table 2. Conversion of CO and selectivities of products at various H<sub>2</sub>/CO ratios.

H <sub>2</sub> /C O	Conversion (%)	Selectivity (%)								
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> CHO	MeOH	EtOH	PrOH	BuOH
1	7.55	11.84	15.01	11.21	-	5.09	8.97	44.9	1.82	1.16
2	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
3	8.01	12.67	12.34	3.94	-	6.97	12.69	48.73	2.13	0.53

4      8.32      14.67      13.05      3.67      -      6.52      13.94      45.57      2.05      0.53

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

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<sup>3</sup> min<sup>-1</sup>, and  $GHSV = 600$  cm<sup>3</sup> gcat<sup>-1</sup> h<sup>-1</sup>,  $X_{CO}$  is 8.10% and  $S_{EtOH}$  and  $S_{CH_4}$  are 51.89% and 10.85%, respectively. In these conditions, MoS<sub>2</sub> catalyst shows obvious favour for EtOH and slight restraint for CH<sub>4</sub>. 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.

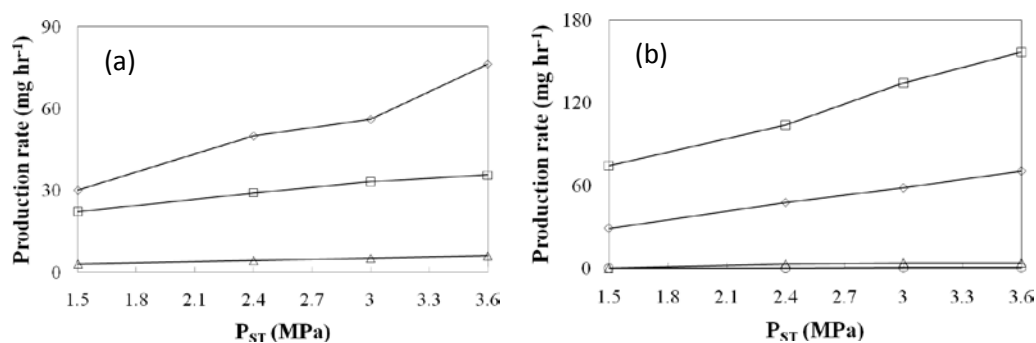


Fig. 5. Production rates of (a) alkane and (b) alcohol products at various pressures via HPCPB-MoS<sub>2</sub> process.  $\diamond$ ,  $\square$ ,  $\triangle$ ,  $\circ$ : C1, C2, C3, C4.

Table 3. Conversion of CO and selectivities of products at various pressures.

$P_{ST}$ (MPa)	Conversion (%)	Selectivity (%)								
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> CHO	MeOH	EtOH	PrOH	BuOH
1.5	4.6	11.84	15.01	11.21	-	-	9.93	50.92	2.47	-
2.4	6.48	12.05	14.04	3.08	-	7.27	11.29	50.00	2.27	-
3.0	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
3.6	9.57	12.46	12.63	2.96	-	3.71	13.94	51.16	2.86	0.28

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

Table 3 illustrates  $X_{CO}$  and S of synthesis products at the four different reaction pressures (reading at 298 K). Setting the reaction at the conditions of  $T = 523$  K,  $H_2/CO = 2$ ,  $Q_G = 300$   $cm^3$   $min^{-1}$ , and  $GHSV = 600$   $cm^3$   $gcat^{-1}$   $h^{-1}$ . As the increased pressure in this study, there are only increasing effects for  $X_{CO}$  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.

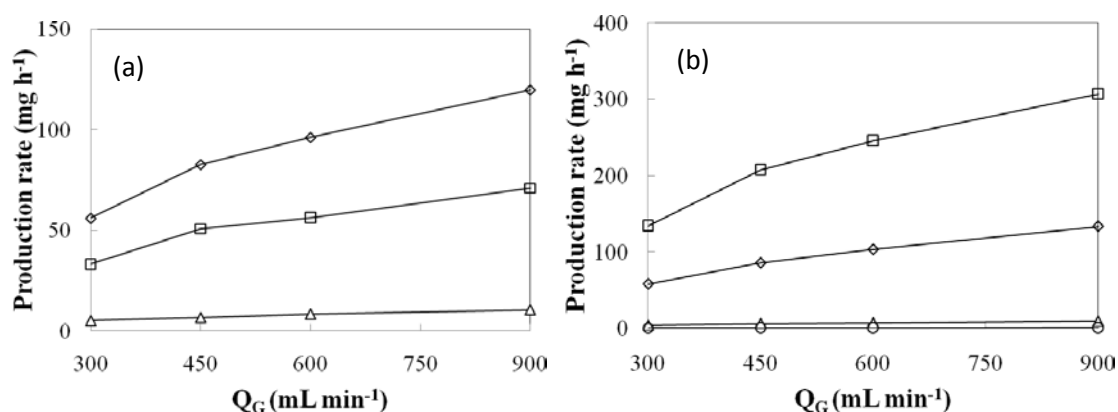


Fig. 6. Production rates of (a) alkane and (b) alcohol products at various flow rates via HPCPB-MoS<sub>2</sub> process.  $\diamond$ ,  $\square$ ,  $\triangle$ ,  $\circ$ : C1, C2, C3, C4.

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  $T = 523$  K,  $H_2/CO = 2$ ,  $P_{ST} = 3$  MPa, and  $GHSV = 300$   $cm^3$   $min^{-1}$ . As the shown in table 4, increasing the flow rate obviously decrease  $X_{CO}$  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.

$Q_G$ ( $mL\ min^{-1}$ )	Conversion (%)	Selectivity (%)								
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> CHO	MeOH	EtOH	PrOH	BuOH
300	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
450	5.44	10.54	12.95	2.52	-	7.54	10.91	52.91	2.37	0.26
600	4.83	10.41	12.18	2.70	-	7.82	11.16	53.14	2.34	0.25
900	4.12	10.25	12.14	2.68	-	8.38	11.39	52.50	2.40	0.26

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

#### 4. Conclusions

In HPFPB system, the main organic products of alkane and alcohols of MoS<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> 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<sub>EtOH</sub>, but also restrains the amount of alkanes formed. Furthermore, it could increase S<sub>EtOH</sub> versus CH<sub>4</sub> while setting the H<sub>2</sub>/CO feed ratio as 2. Considering the effects of P<sub>ST</sub> and Q<sub>G</sub>, 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<sub>CO</sub> 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<sub>2</sub>/CO = 2, higher pressure, and lower flow rate to reach the purpose of obtaining higher X<sub>CO</sub> and outstanding S<sub>EtOH</sub>.

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