

# Methanol synthesis from bio-hydrogen

Kuo-Hsin Lin<sup>a</sup>, Chen-Yeon Chu<sup>a, b</sup>, Chiu-Yue Lin<sup>b</sup>, Alex C.C. Chang<sup>a, b, \*</sup>

<sup>a</sup> Department of Chemical Engineering, Feng Chia University

<sup>b</sup> Green Energy Development Center, Feng Chia University

\*Email: acchang@fcu.edu.tw

## Abstract

The aim of this study is using bio-hydrogen to produce methanol through the methanol synthesis. The bio-hydrogen is obtained from the effluent gas of anaerobic fermentation process, where the effluent gas is composed of H<sub>2</sub> (25-75%) and CO<sub>2</sub>. The fair purity of hydrogen always limited its applications; therefore, the aim of this study is to deal with this problem. Furthermore, the process is an exothermic reaction and it proceeds under volume contraction so that the higher methanol yield must be obtained at low temperature and high pressure.

The commercial catalyst MDC-3 (Cu/Zn/Al<sub>2</sub>O<sub>3</sub>) is employed in the preliminary experiments at 250 °C, 30 bar, 2400 ml/g-hr and with a fixed H<sub>2</sub>/CO<sub>2</sub> ratio of 3. The results show the reaction is reaching stability in the first 30 minutes with an average CO<sub>2</sub> conversion of 8.8% and methanol yield of 19.2%. It also found a trace of dimethyl ether (less than 0.1%) and CO (2.5%) produced during the course of reaction, where the later one is generated through the reverse water gas shift reaction. Consequently, the overall reaction at least involved three reactions as following: (1) CO<sub>2</sub> hydrogenation reaction; (2) CO hydrogenation reaction; (3) reverse water gas shift reaction. The thermodynamic equilibrium is also evaluated by the MATLAB software from 10-30 bar and 200-300 °C.

Keywords: Bio-hydrogen, Methanol synthesis

NSC Project no.: NSC 101-2922-I-035-011, NSC 99-2632-E-035-001-MY3

## 1 Introduction

Green house gas emission has caught much more attentions around the world and leading to the global warming effects. In the past decades, fossil fuel was the major energy resource and released considerable amount of carbon dioxide during its usage. Therefore, seeking for the alternatively energy resource is the most promising issue for the present time. Bio-energy is considered as one of the most potential energy resource among all renewable energies. Conventionally, bio-energy can be produced from the thermal-chemical or the biological processes. In the recent years, our group devoted in integrating both of the processes and developed a new one which could not only effectively produce bio-energy (hydrogen, methane, ethanol, butanol, etc.) but also make full use of biomass as well as agricultural waste. Unfortunately, the fair purity of hydrogen (25-75 %) [1] always limits its application and the purification of hydrogen is not widely developed yet. Therefore, in this study the methanol synthesis using bio-hydrogen is considered as an alternative chance.

Methanol synthesis ( $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ ) was proposed by BASF in 1923 [2], which firstly introduced the zinc/chromite catalyst for the industrial application. The catalyst showed a low activity and consequently the process had to be carried out at high temperatures and pressures in order to reach a profitable yield of methanol (573-633K, 25 MPa). Although it showed low activity for methanol synthesis, it was used and improved for a long period until the 1950s. For the present time, the most favourable catalyst is copper/zinc oxide/alumina catalyst. The copper/zinc system was characterized by a particularly high activity [3-5] and the addition of alumina was found to be able to stabilize the thermal resistance of the catalyst [5].

In this work, methanol synthesis was carried out at 250 °C with employing commercial catalyst, MDC-3, as the promoter. The feedstock was composed of H<sub>2</sub> and CO<sub>2</sub>, where its composition was referred to the effluent gas of anaerobic process. The thermodynamic equilibrium is also evaluated by MATLAB software in pressure range of 10-30 bars and temperature range of 200-300 °C.

## 2 Experimental

The schematic diagram of the experimental apparatus is shown in Fig. 1. The reaction was carried out in a fixed-bed tubular stainless steel reactor (O.D. = 1/2"), with 1 g of the catalysts (MDC-3) being placed at the center of the reactor between two quartz wool and fixed at temperature of 250 °C by a tubular furnace. The pressure was controlled (10, 20 and 30 bars) by a back pressure regulator, which was installed at the end of reactor. Before the reaction, the catalyst was reduced in situ with 10% H<sub>2</sub>/Ar stream for 2 hours. The Space velocity of feedstock was fixed at 3600 ml/g-hr and the composition was varied from H<sub>2</sub>/CO<sub>2</sub> ratio of 1, 2 and 3. Every test was proceed for 15 hours and the effluent gas was also heated at 150 °C to prevent condensation. Gas chromatograph (SRI 8610C) was equipped with a thermal conductivity detector (TCD) and a flame ionization detector to analyze the gas products. The definition of conversion, selectivity and concentration was described by equations as shown below,

$$X_i = \frac{n_i - n_i^0}{n_i^0} \times 100\% \quad , i = CO_2, H_2 \quad (1)$$

$$S_{MeOH} = \frac{n_{MeOH}}{n_{CO_2}^0 - n_{CO_2}} \times 100\% \quad (2)$$

$$C_i = \frac{n_i}{N_T} \times 100\% \quad (3)$$

where  $X_i$  stands the conversion of  $i$  species,  $n_i$  stands moles of  $i$  species at time  $t$ ,  $S$  stands the selectivity,  $C_i$  stands the concentration of  $i$  species, and  $N_T$  represents total moles of all species.

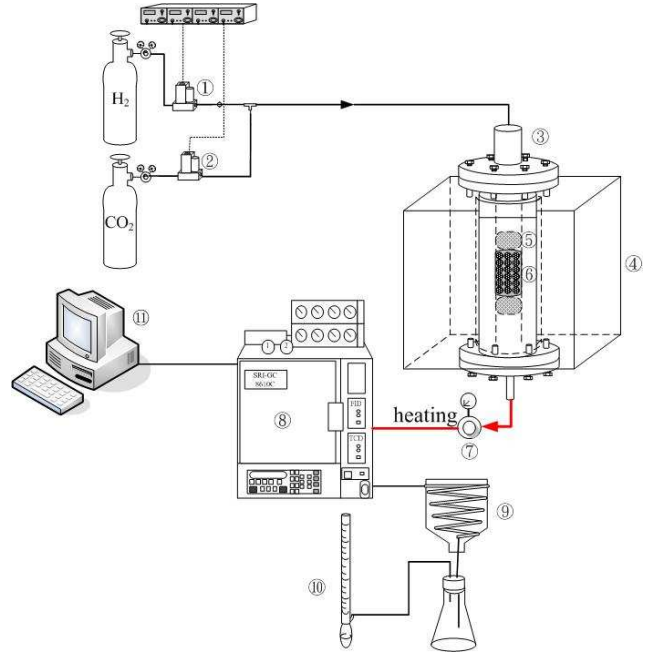
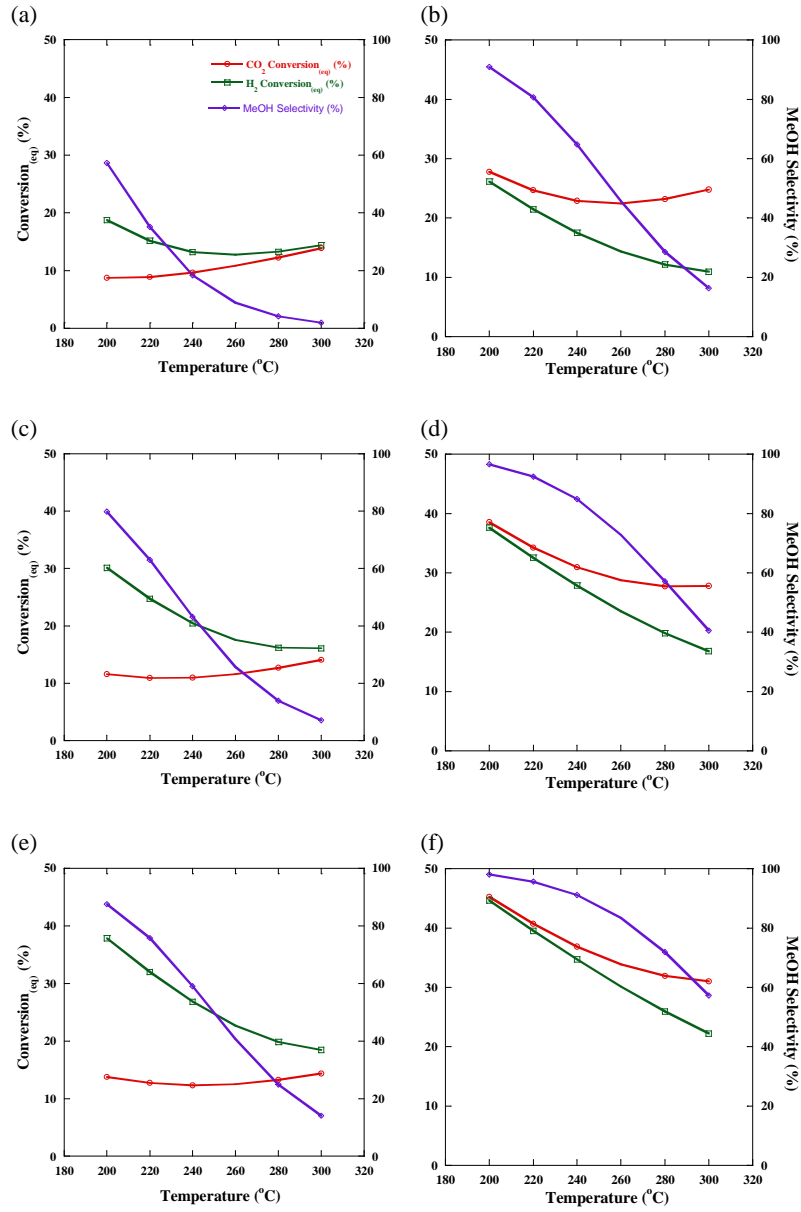


Fig. 1. Schematic diagram of this study: (1) H<sub>2</sub> mass flow meter, (2) CO<sub>2</sub> mass flow meter, (3) reactor, (4) furnace, (5) glass wool, (6) catalyst, (7) back pressure regulator, (8) gas chromatograph, (9) cooling device, (10) soap-bubble flow meter, (11) personal computer.

## 3 Results and discussion

In this study, the thermodynamic equilibrium for methanol synthesis was computed by the MATLAB software in the temperature range of 200-300 °C, pressure range of 10-30 bar and H<sub>2</sub>/CO<sub>2</sub> ratio of 3 and 1. The computation results were shown in Fig. 2. The computation showed that the selectivity of methanol decreased with increasing temperature in all cases. For the cases of H<sub>2</sub>/CO<sub>2</sub> ratio of 1, the equilibrium conversion of CO<sub>2</sub> showed opposite trend with selectivity, which was suggested by the competition of side reactions. Furthermore, the computation showed the reaction indeed depended on the pressure, temperature and feedstock ratio. Increasing the feedstock ratio from H<sub>2</sub>/CO<sub>2</sub> ratio of 1 to 3, the conversion of carbon dioxide and hydrogen increased obviously as well as methanol selectivity. It also seemed that the reaction was depending much more on the feedstock ratio than pressure. Table 1 shows the results of experimental runs. Generally, CO<sub>2</sub> conversion was increased with increasing pressure as well as increasing H<sub>2</sub>/CO<sub>2</sub> ratio. However, the conversion of hydrogen and methanol selectivity did not follow this trend. The experimental runs showed the best methanol



**Fig. 2.** Computation results of equilibrium conversion of CO<sub>2</sub> and H<sub>2</sub>, and selectivity of methanol: (a) 10 bar, H<sub>2</sub>/CO<sub>2</sub> = 1, (b) 10 bar, H<sub>2</sub>/CO<sub>2</sub> = 3, (c) 20 bar, H<sub>2</sub>/CO<sub>2</sub> = 1, (d) 20 bar, H<sub>2</sub>/CO<sub>2</sub> = 3, (e) 30 bar, H<sub>2</sub>/CO<sub>2</sub> = 1, (f) 30 bar, H<sub>2</sub>/CO<sub>2</sub> = 3.

**Table 1.** Results of experimental runs.

H <sub>2</sub> /CO <sub>2</sub>	Pressure (bar)	X <sub>CO<sub>2</sub></sub> (%)	X <sub>H<sub>2</sub></sub> (%)	S <sub>MeOH</sub> (%)
1	10	13.97	11.89	N/D
1	20	13.25	15.20	9.71
1	30	7.24	14.10	22.21
2	10	15.22	5.38	N/D
2	20	7.66	8.94	40.50
2	30	15.89	8.15	18.67
3	10	19.84	2.78	N/D
3	20	29.39	7.91	12.43
3	30	23.17	7.26	20.34

Reaction condition, 250 °C, space velocity of 3600 ml/g-cat.-hr.

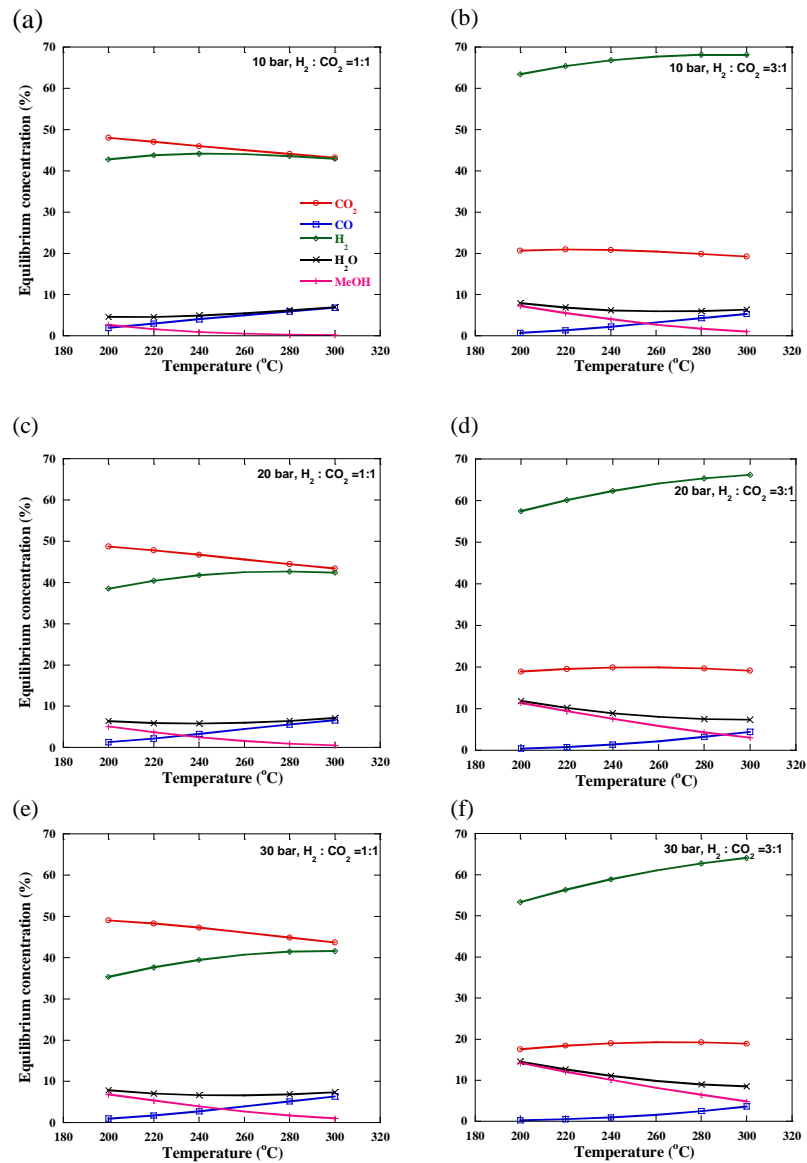
N/D, not detected.

**Table 2.** Species concentration of the experimental runs.

$H_2/CO_2$	Pressure (bar)	Concentration (%)				
		$CO_2$	$H_2$	CO	MeOH	$H_2O$
1	10	45.83	45.93	4.20	N/D	4.03
1	20	47.66	43.37	4.08	0.70	4.18
1	30	49.29	42.93	3.00	0.78	3.70
2	10	28.09	63.84	4.12	N/D	3.94
2	20	30.01	60.93	3.89	0.87	4.30
2	30	32.35	59.03	3.35	1.11	4.13
3	10	17.39	74.73	3.97	N/D	3.90
3	20	19.13	71.78	3.69	0.98	4.40
3	30	21.20	69.97	3.28	1.28	4.25

Reaction condition, 250 °C, space velocity of 3600 ml/g-cat.-hr.

N/D, not detected.



**Fig 3.** Computation results of equilibrium concentration: (a) 10 bar,  $H_2/CO_2 = 1$ , (b) 10 bar,  $H_2/CO_2 = 3$ , (c) 20 bar,  $H_2/CO_2 = 1$ , (d) 20 bar,  $H_2/CO_2 = 3$ , (e) 30 bar,  $H_2/CO_2 = 1$ , (f) 30 bar,  $H_2/CO_2 = 3$ .

selectivity was 40.50 % at the condition of 20 bar and  $H_2/CO_2$  ratio of 2. It had to mention that for the case of 10 bar ( $H_2/CO_2 = 1, 2$  and 3) it did not detected any methanol from FID detector due to its concentration was out of detection.

Fig. 3 shows the computation of equilibrium concentration of each species. Methanol concentration was decreased with increasing temperature in all cases since the reaction was exothermic. The computation showed again that methanol synthesis was depending much more on  $H_2/CO_2$  ratio than pressure. CO concentration was highly depending on temperature due to the reverse water gas shift reaction, which was also the main side reaction. Table 2 shows the species concentration of experimental runs. For the case of same  $H_2/CO_2$  ratio, CO concentration was decreased with increasing pressure indicating that reverse water gas shift reaction was apparently restricted by pressure. However, it also could be explained by the weakness competition comparing with  $CO_2$  hydrogenation reaction.  $H_2O$  concentration showed an opposite trend with CO, which was suggested that the reaction accompanied with CO hydrogenation reaction so that CO was further reacted with hydrogen to produce methanol. Methanol concentration was increased slightly with both increasing  $H_2/CO_2$  ratio and pressure.

#### 4 Conclusion

In this study, the methanol synthesis was carried out and computed under mild conditions (10-30 bar). The feedstock was modulated according to anaerobic fermentation process. The experimental results showed the whole reaction took place under kinetic control regime. Furthermore, the reaction was much more depending on feedstock ratio than reaction pressure. The competition intensity of side reaction also affected the product distribution. Computation results show the reaction was favored under high pressure condition, which was also consistent with the experimental ones. Furthermore, it was difficult to determine the optimal condition both from computations and experiments. In general, the optimization was always evaluated and determined by the degree of yield. However, the computation was based on the feedstock ratio, temperature and pressure, and irrelevant to the feedstock rate and production rate so the yield could not

be determined. In the present work, we proposed a possibility of utilizing bio-hydrogen which also benefit to climate and environment.

#### Acknowledgments

The authors like to thank the National Science Council of the Republic of China under the contract No. NSC 101-2922-I-035-011, NSC 99-2632-E-035-001-MY3 and Feng Chia University under the contract No. FCU-10G27101 for their financial support.

#### References

- [1] Chang A.C.C., Tu Y.H., Huang M.H., Lay C.H., Lin C.Y. Hydrogen production by the anaerobic fermentation from acid hydrolyzed rice straw hydrolysate. *International Journal of Hydrogen Energy* 2011;36:14280-14288.
- [2] Asinger F. *Methanol-Chemie-und Energierohstoff*. Springer Verlag 1986.
- [3] Macnaughton N.J., Pinto A., Rogerson P.L. Development of methanol technology for future fuel and chemical markets. *Energy progress* 1984;4:232-241.
- [4] Dybkjaer I. Design of ammonia and methanol synthesis reactors, in *ASI-NATO Conference: Chemical Reactor Design and Technology* 1985:London (Ontario):795-819.
- [5] Dry R.J. Possibilities for the development of large-capacity methanol synthesis reactors for synfuel production. *Industrial & Engineering Chemistry Research* 1988;27:616-624.