



THERMODYNAMICS AND KINETICS STUDY OF CH₃OK PREPARATION FROM KOH AND CH₃OH

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ABSTRACT

Potassium methoxide is the catalyst for methanol carbonylation process with the CO. This catalyst is prepared by reacting potassium hydroxide with methanol at a temperature of 25-50 °C. Besides the reaction temperature, preparation of catalyst was influenced by the composition of the feed of reactants. Chemical composition in the liquid phase were analyzed using gas chromatography method, and composition of vapour phase was predicted using UNIFAC model. Concentration of CH₃OK in the catalyst solution increases with increasing molar ratio of feed and temperature. Yield of CH₃OK decrease if molar ratio of feed increased. The highest concentration of CH₃OK achieved at molar ratio of feed 0.039 and temperature 50°C. Reaction rate for alcoholysis of potassium hydroxide is a function of the concentration of potassium hydroxide. The activation energy was found 17.81 kJ/mole, and pre-exponential factor was 26.3 min⁻¹.

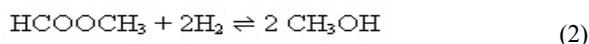
Keywords: potassium methoxide, alcoholysis, chemical and vapour-liquid phase equilibrium, kinetics.

1. INTRODUCTION

In line with our research on biomass utilization, methanol is one of prospective biomass-derived chemical. Methanol may be used as a fuel or converted further to dimethyl-ether as a substitute of LPG. Commercial production of methanol is now carried out a high temperature and pressure (250-300 °C and 50-100 bar) using a CuO/ZnO catalyst. Since methanol synthesis is an exothermic reaction, the conversion is low at a higher temperature. Therefore many efforts to develop a catalyst giving a reasonable rate of methanol synthesis at a lower temperature [1].

Biomass can be converted into bio-syngas (biomass-derived synthesis gas containing CO and H₂) via gasification process. Unfortunately availability of biomass are usually in non-economically amount. Therefore, an appropriate technology for biomethanol synthesis has been considered to be developed to have the following characteristics: low temperature and low pressure, as well as economically in a small scale.

The low temperature synthesis of methanol from biomass synthesis gas via methyl formate is one of promising process and expected can be integrated with small scale gasifier. The synthesis of methanol consist two step of reaction, the first is carbonylation of methanol to methyl formate, and the second are hydrogenolysis of methyl formate become two molecule of methanol as shown with equation (1) and (2).

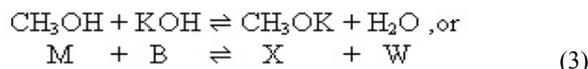


Potassium methoxide and metallic copper are used as catalyst for the carbonylation of methanol and the successive hydrogenolysis of methyl formate, respectively.

There are several methods for the preparation of potassium methoxide. The summary of methods of potassium methoxide preparation shown in the Table-1.

One of these methods involves the reaction of metallic potassium with a methanol to form the potassium methoxide and hydrogen. The second method involves the reaction of potassium carbonate with a methanol to form the potassium methoxide and potassium bicarbonate. The solution of the potassium methoxide and potassium bicarbonate is concentrated so that potassium bicarbonate precipitates. The bicarbonate is isolated, calcined to form the carbonate and re-used in the reaction with the alcohol. The third method involves the reaction of potassium hydroxide with a methanol to form potassium methoxide and water. The water formed is continuously removed from the solution system using adsorbent. The adsorbent can be re-used after activated at high temperature.

Preparation of potassium methoxide from potassium hydroxide and methanol are more interesting to develop (see eq. (3)). This method has some advantages over alcoholysis of alkali metal and alkali carbonate, such as potassium hydroxide are cheaper raw material than metal of potassium and potassium carbonate.



Reaction of potassium hydroxide and methanol to form potassium methoxide and water is a reversible reaction. Komers *et al* [5] and Platonov *et al* [6] reporting the thermodynamic behaviour of potassium methoxide synthesis from potassium hydroxide and methanol at 25 °C. However, these study is not a comprehensive thermodynamic analysis on this process. Therefore, this paper describes the study of thermodynamics is more complete. In addition, the paper also comes with a discussion of the kinetics of the reaction of alcoholysis of potassium hydroxide. Both of these studies are needed to optimize the potassium methoxide preparation for carbonylation process in methanol synthesis.

**Table-1.** Summary of synthesis of various potassium methoxide.

No.	Author	Method of preparation	Ref.
1	Chandran et al (2006)	$M + R-OH \rightarrow R-OM + \frac{1}{2} H_2$ [M= Na; and R= -CH ₃ ; -C ₂ H ₅ ; -C ₃ H ₇]	[2]
2	Patent RU 2178402	$M_2CO_3 + 2ROH \rightarrow ROM + MHCO_3$ [M= Li; Na; K and R=-CH ₃ ; -C ₂ H ₅]	[3]
3	Mitchel et al (1969)	$MOH + ROH \rightleftharpoons R-OM + H_2O$ [M= Li; Na;K and R= -CH ₃ ; -C ₂ H ₅]	[4]

2. EXPERIMENTAL

Potassium hydroxide and methanol were used from CV. Bratachem. Before used for potassium methoxide preparation, the water concentration in methanol was determined by the gas chromatography method and it did not exceed 0.23 %-volume (2291 ppmv). Water in the potassium hydroxide (KOH) was determined by drying method. Temperature of drying set at 105 °C, and water in the KOH is not exceed 5%-mass.

The reaction of alcoholysis of potassium hydroxide was carried out using a 60 mL sample vial containing a magnetic stirrer and hermetically sealed. The amount of methanol used in each experiment was 30 mL. Methanol is then charged into the vial, then heated to the desired operating temperature. After the temperature of the solution reaches to the desired condition, a further amount of KOH charged into the vial, and then the solution stirred at 700 rpm. The solution was continuously stirred for 1 h at the level temperature.

The liquid sample were analyzed using thermal conductivity of gas chromatography (GC) Shimadzu 14B. The column of GC filled with Porapak-Q. The temperatures of the column oven, injector and detector were 150 °C, 200 °C and 200 °C, respectively. Argon (99.9%) was used as a carrier-gas with flow rate of 15 cm³.s⁻¹. The GC sample from liquid a phase was taken using Hamilton micro syringe, and sample volumes about 0.5 micro liter. The liquid sampling at an interval of about 20 min.

Liquid sample calibration performed using water + methanol solutions of known concentrations. The area of the water peak was normalized to the methanol peak. Calculation of the quantity of water in a sample was made based on the ration of the peak areas of water and methanol. Concentration of KOH, CH₃OH and CH₃OK calculated from water formation from reaction. Composition at equilibrium condition in vapour phase calculated based on approaching the UNIFAC model. Effect of KOH and CH₃OK in the system to vapour-liquid equilibrium are neglected.

3. RESULT AND DISCUSSION

a) Thermodynamics study

Figure-1 shows an example of the time course of KOH, CH₃OK and H₂O concentration during the run using molar ratio of feed (mole of KOH/mole of CH₃OH) is

0.012 at 50 °C. In this run, the initial concentration of water is 3124 ppmv. This water come from methanol and potassium hydroxide as a reactant. The progress of concentration of water in liquid sample were analyzed by GC. The concentration of water increased and reach of equilibrium after 20 minute. Also the KOH concentration decreased rapidly due to consumption of KOH to form CH₃OK. Can be seen in the curve, the reactants and the products have concentrations which do not change with time. This system is called to be in chemical equilibrium.

The chemical equilibrium composition at various temperature of the alcoholysis of potassium hydroxide reaction was carried out with three different initial compositions of the reaction mixture. The chemical equilibrium composition in liquid phase shown with Table-2. The concentration of CH₃OK increases with increasing molar ratio of feed and temperature. However, in Figure-2 we can see the increasing of molar ratio of feed, the curve of yield of CH₃OK become decreased (yield of CH₃OK calculated from mole CH₃OK of experiment divided by CH₃OK if all KOH converted to CH₃OK). This is caused by the equilibrium is shifted to the reverse direction. Increasing temperature and decreasing molar ratio of feed can be advantageous to the yield of CH₃OK. The highest concentration of CH₃OK achieved at molar ratio of feed 0.039 and temperature 50 °C. However, at this condition there are KOH still not conversion. For achieving conversion of KOH to 100%, the reaction temperature should be more then high from 50 °C.

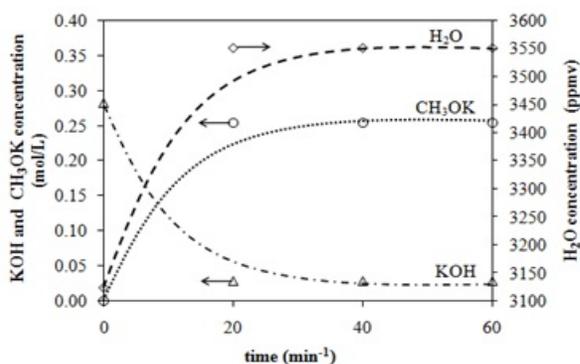


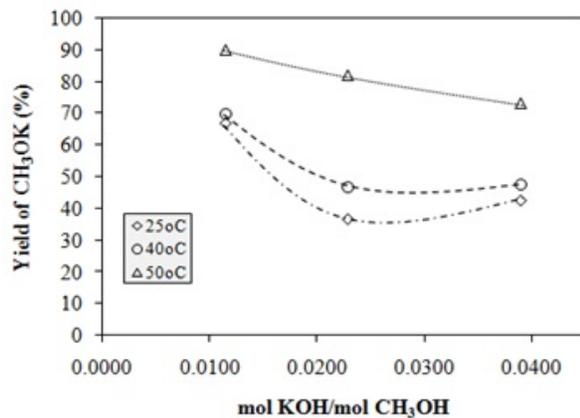
Figure-1. Time course of KOH, CH₃OK and H₂O during the run. Feed molar ratio (KOH/CH₃OH)= 0.023; Temp.=25 °C.

**Table-2.** Chemical and liquid-vapour phase equilibrium of KOH+CH₃OH+CH₃OK+H₂O system.

No.	Temp. (°C)	molar ratio of Feed (mol/mol)*	Liquid phase composition (%-wt)				Vapour phase composition (%-wt)**	
			KOH	CH ₃ OH	CH ₃ OK	H ₂ O	CH ₃ OH	H ₂ O
1	25	0.012	1.09	96.91	1.64	0.81	99.67	0.33
2		0.023	2.43	94.88	1.76	0.93	99.62	0.38
3		0.039	3.64	91.51	3.38	1.47	99.38	0.62
4	40	0.012	0.59	96.88	1.71	0.83	99.62	0.38
5		0.023	2.05	94.67	2.23	1.05	99.51	0.49
6		0.039	3.31	91.33	3.78	1.58	99.24	0.76
7	50	0.012	0.20	96.65	2.20	0.95	99.53	0.47
8		0.023	0.70	93.89	3.92	1.49	99.24	0.76
9		0.039	1.71	90.41	5.79	2.09	98.91	1.09

* mole of KOH/mole of CH₃OH

**Calculated using UNIFAC model with composition in liquid phase only methanol and water

**Figure-2.** Effect molar ratio of feed and temperature to yield of CH₃OK.

The vapour-liquid equilibrium were determined after chemical equilibrium was reached. Vapour-liquid equilibrium calculated using approach of model. Vapour-liquid parameter were calculated using the UNIFAC group contribution model. This model is can be used for binary and multicomponent system. The UNIFAC method provides a good fit to experimental vapour-liquid equilibrium for methanol-water system data. The group parameters and procedure of calculation of the UNIFAC model for calculating the equilibrium in the methanol-water system were taken from [7]. From calculation result, water concentration in the vapour phase increased with increasing concentration of water in the liquid phase.

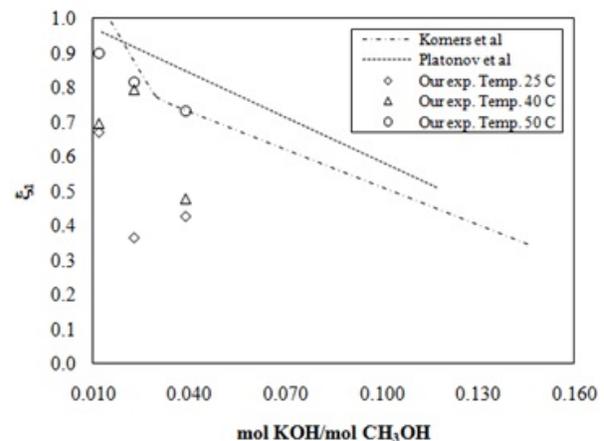
$$Kc = \xi_1 \left(\frac{n_{w_0}}{n_{B_0}} + \xi_1 \right) / \left(\left(\frac{n_{M_0}}{n_{B_0}} - \xi_1 \right) (1 - \xi_1) \right) \quad (4)$$

$$\xi_1 = \frac{\xi}{n_{B_0}} ; |\xi| \in \langle 0; 1 \rangle \quad (5)$$

With ξ_1 is the equilibrium extent of the reaction related to 1 mol of pure KOH, n_{w_0} is initial number of moles of water, n_{B_0} is initial number of mole of potassium hydroxide, n_{M_0} is initial number for methanol and ξ is the equilibrium extent of the reaction defined as:

$$n_i = n_{i_0} + v_i \xi \quad (6)$$

Where v_i is stoichiometric coefficient of component i , n_i is the equilibrium and n_{i_0} initial number of moles of the component i .

**Figure-3.** Dependence of the equilibrium extent of the reaction (ξ_1).

The equilibrium extent of the reaction (ξ_1) as a function of molar ratio of feed shown on Figure-3. The equilibrium extent of the reaction (ξ_1) decreased with the increasing of molar ratio of feed. Our experiments on



potassium methoxide preparation were not as good as those obtained by Komers *et al* [5] and Platonov [6]. We guessed that this is caused our feed contain more water.

The equilibrium constants at various molar ratio of feed and temperature from calculation using equation (4) shown by Figure-4. From these curve can be seen, the equilibrium constant for molar ratio of feed 0.012 and 0.039 very close at the same temperature. However, the equilibrium constants for the molar ratio of feed 0.023 is very far from the two other feed compositions.

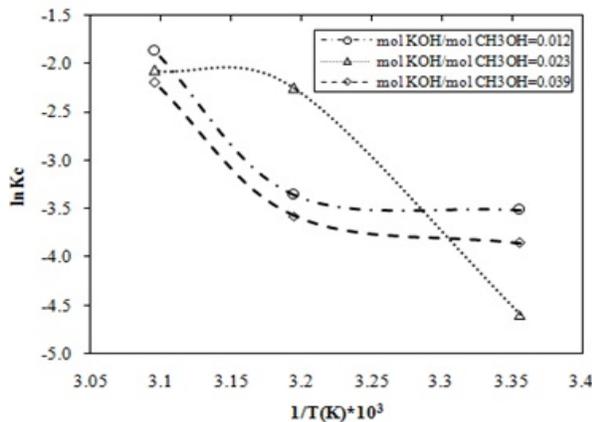


Figure-4. Equilibrium constants as temperature function.

The equilibrium constants was correlated with reaction temperature using a least square regression. The equation used for this correlation is:

$$\ln(K_c) = A + \frac{B}{T} \quad (7)$$

The result of regression is:

$$\ln(K_c) = 17.12 - \frac{6438.3}{T} \quad (8)$$

Deviation of the equilibrium constants from the model compared with the experiment did not exceed 13%.

b) Kinetics study

Reaction potassium hydroxide and methanol is reversible reaction under the operating condition used in this work. The knowledge of kinetics about this reaction is not available in the literature. Therefore, we proposed the rate of the reaction for alcoholysis of potassium hydroxide. The reaction rate is assumed to be a function of the concentration of potassium hydroxide and methanol as shown in equation (9) as below.

$$-r_{KOH} = k_0 C_{KOH}^a C_{CH_3OH}^b \quad (9)$$

where $-r_{KOH}$ is the reaction rate of KOH (mole/(L.minute)), C_{KOH} and C_{CH_3OH} is the concentration of KOH and CH_3OH (mole/L), a and b are the reaction orders, and k_0 is rate constant. Then, we simplify the equation (9) with assumption that the reaction was first order with respect to the KOH and CH_3OH concentration.

Methanol concentration during the reaction is almost unchanged, due to the concentration of the methanol made excessive. Therefore, the effect of methanol concentration is considered constant, and equation (9) can be simplified into the following equation (10).

$$-r_{KOH} = k C_{KOH} \quad (10)$$

An initial rate technique was used to determine the kinetic parameter. The initial rate can be calculated from the slope of the potassium hydroxide concentration-time curve in the first twenty minute (see Figure-5).

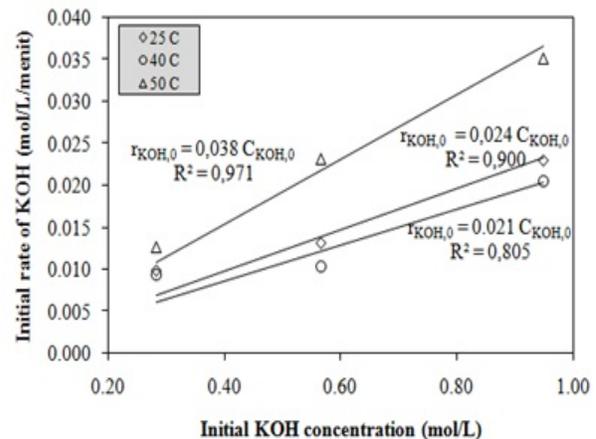


Figure-5. Initial rate of KOH as a function initial KOH concentration.

The value of k in this work was calculated at various temperatures. Values of k were obtained by linier regression of equation (10) for different initial hydroxide concentration. The values of rate constant and activation energy for reaction were evaluated from the Arrhenius plot in Figure-6. The activation energy was 17.81 kJ/mole, and pre-exponential factor was 26.3 min^{-1} .

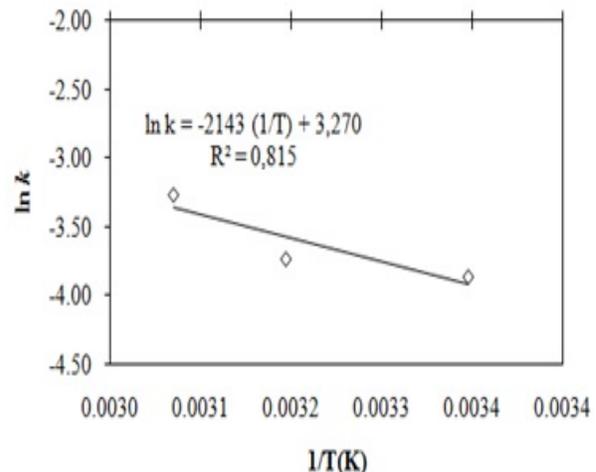


Figure-6. Rate constant as a function temperature.



4. CONCLUSIONS

Alcoholysis of potassium hydroxide to form potassium methoxide was studied. From thermodynamic study, the concentration of CH_3OK increases with increasing molar ratio of feed and temperature. However, increasing of molar ratio of feed make yield of CH_3OK become decreased. Composition of vapour phase was predicted using UNIFAC model. Constants of chemical equilibrium were calculated from experiment data. From kinetics study we proposed reaction rate is a function of the concentration of potassium hydroxide. The activation energy was found 17.81 kJ/mole, and pre-exponential factor was 26.3 min^{-1} .

Thermodynamics. 7th edition. Mc Graw Hill. Asia. pp. 791-797.

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