Free fatty acid esterification with methanol catalyzed by Amberlyst BD 20

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Abstract: Without proper treatment, waste cooking oil (WCO) might become an environmental problem and a food safety problem. WCO can be converted to biodiesel before its free fatty acid (FFA) is removed by esterification with methanol using acid catalyst. In order to eliminate downstream separation problems, liquid catalysts are not used. Instead, solid acid catalyst, Amberlyst BD 20 is used as the catalyst. The effects of methanol to FFA ratio, catalyst dose, water content, and reaction temperature were investigated. The experimental results are in good agreement with those predicted by a proposed kinetic model based on Eley–Rideal mechanism.

Keywords: Esterification, Free fatty acid, Kinetics.

1. Introduction

Large amounts of waste cooking oil (WCO) are generated daily from restaurants and night markets in Taiwan. Without proper treatment, such waste cooking oil might become an environmental problem when dumped randomly. It may also cause a food safety problem if it is misused. A project is being conducted to remove the FFA contained in the WCO using solid acid catalyst, followed by converting the WCO to biodiesel using solid base catalyst. Various solid acid catalysts are being prepared and a kinetic model indispensable for reactor design is also being developed. Experimental work was done using commercial catalyst Amberlyst BD 20 and the data were analyzed by a kinetic model derived from our previous methodology1.

2. Experimental

The reaction mixtures containing oleic acid, methanol, catalyst, and water were prepared and placed in aluminum alloy air-tight containers as reactors. After a reaction chamber reached the desired temperature, all the reactors were placed and fixed on a plate that rotated at a constant speed. After certain time, the plate rotation stopped, all the reactors were taken and immersed in an ice bath to quench the reaction. The remaining acid value in the oil phase of each reactor was measured by Automatic Potentiometric Titrator (model AT-710, Kyoto Electronics Manufacturing Co., Ltd). The experimental factors such as methanol to oleic acid molar ratio, catalyst dose, water content, and temperature were varied and the data were analyzed by a proposed kinetic model.

3. Results and discussion

The oleic acid esterification with methanol is assumed to follow the Eley–Rideal mechanism:

$$M + S \underset{k_{10}}{\overset{k_{01}}{\longleftrightarrow}} MS \qquad \text{Adsorption of methanol}$$

$$MS + A \underset{k_{21}}{\overset{k_{12}}{\longleftrightarrow}} WS + E \qquad \text{Reaction of oleic acid (A) with adsorbed methanol}$$

$$WS \underset{k_{32}}{\overset{k_{23}}{\longleftrightarrow}} W + S \qquad \text{Desorption of water (W)}$$

Without assuming which step is the rate determining one, the rate equation of esterification was readily derived by our previous methodology:[1]

$$r = \frac{k_a K_M (C_A C_M - \frac{K_W C_E C_W}{K_M K_S})}{1 + K_M C_M + K_W C_W + k_c C_E (1 + K_M C_M + \frac{k_b}{k_c} K_W C_W) + k_b C_A (1 + \frac{k_c}{k_b} K_S K_M C_M + K_W C_W)}$$

where the lumped kinetic parameters are defined as

$$k_a \equiv k_{12} C_{cat} \qquad K_M \equiv \frac{k_{01}}{k_{10}} [=] \frac{L}{mol} \qquad K_W \equiv \frac{k_{32}}{k_{23}} [=] \frac{L}{mol} \qquad K_S \equiv \frac{k_{12}}{k_{21}} \qquad k_b \equiv \frac{k_{12}}{k_{10}} \qquad k_c \equiv \frac{k_{21}}{k_{23}}$$

The rate equation was used to calculate the batch conversion as function of time and the lumped kinetic parameters was obtained from fitting the experimental conversions to the model predictions. As is shown by Figure 1 to 2, the experimental results are in good agreement with those predicted by the proposed kinetic model based on Eley–Rideal mechanism.

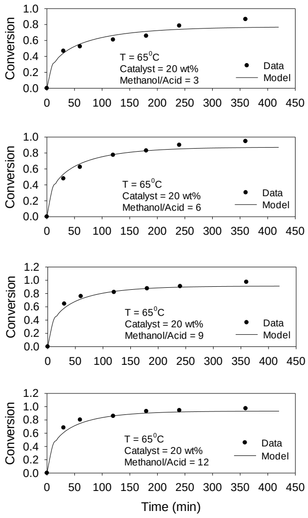

Figure 1. Effect of methanol To acid ratio.

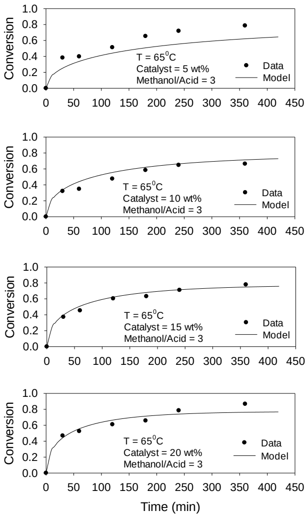

Figure 2. Effect of catalyst dose.

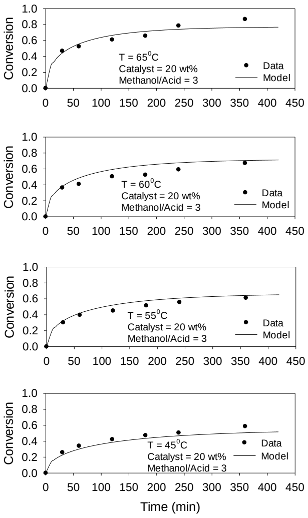

Figure 3. Effect of temperature.

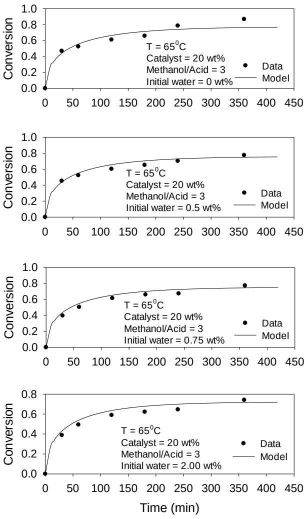

Figure 4. Effect of initial water content.

From the lumped kinetic parameters obtained at different temperatures, the activation energy of each step can be calculated and the results are shown in Table 1. Compared with the value of the activation energy of each step, the surface reaction step cannot be assumed as the sole rate determining step.

Table 1. Activation energy of each reaction step.

Step	Adsorption of methanol	Desorption of methanol	Forward surface reaction	Reverse surface reaction	Desorption of water	Adsorption of water
Activation energy	E_{01}	E_{10}	E_{12}	E_{21}	E_{23}	E_{32}
Value, kJ/mol	69.5	77.7	79.9	78.4	78.5	5.9

4. Conclusions

Amberlyst BD 20 was used as the catalyst for oleic acid esterification with methanol and the experimental results showed the esterification conversion increased with increasing methanol to acid ratio, catalyst dose, or reaction temperature whereas decreased with increasing initial water content. The conversion data were in good agreement with those predicted by a proposed kinetic model based on Eley–Rideal mechanism.

References

1. J.-M. Chern, Ind. Eng. Chem. Res. 39 (2000) 4100.