Kinetic study of triglyceride transesterification with methanol by calcium oxide catalyst

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Abstract: A new kinetic model for catalytic transesterification of oil with methanol by calcium oxide catalyst to yield biodiesel was developed in this study. The network reduction technology was applied by constructing all possible reaction pathways and without assuming any step is rate determining. The kinetic model derived was validated with fitting the kinetic parameters by experimental data we performed and those retrieved from literatures. Results show the kinetic model we proposed can describe the catalytic transesterification well for supporting the core information for process design.

Keywords: Transesterification, Biodiesel, Kinetic model

1. Introduction

Biodiesel as an alternative renewable fuel has become an important issue due to the shortage of petroleum energy. The most common way to produce biodiesel is catalytic transesterification of oil with methanol to yield fatty acid methyl esters and glycerol. Nowadays, using waste oil as the resource of oil has become a new trend for environmental concerns. A suitable kinetic model is necessary for biodiesel process design for preventing the deviations of design. However, we found some kinetic models in the literatures are simply empirical expressions or do not meet thermodynamic consistence. In this study, a new kinetic model was proposed by reaction network reduction techniques. We consider all possible catalytic reaction pathways and without assuming which is rate determining step. After the rate model was developed, experimental data we performed and some other data retrieved from the literatures were reanalyzed with the new model to validate the proposed kinetic model.

2. Theoretical

The main reaction of transesterification of triglyceride with methanol by calcium oxide catalyst is shown in Fig. 1. Since it is a heterogeneous catalytic reaction and the mechanism is complicated, we proposed a three-cycles reaction network after surveyed most information from literatures, as shown in Fig. 2. Methanol was adsorbed onto active site of calcium oxide catalyst in the first step. Then Triglyceride can react with adsorbed methanol and release diglyceride and biodiesel which indicated as reaction r_1 in Fig. 2. The released diglyceride can also react with adsorbed methanol and release monoglyceride and biodiesel indicated as reaction r_2. Finally, the released monoglyceride can also react with adsorbed methanol and release glycerin and biodiesel indicated as reaction r_3. The occupied active site will return to free active site for further reaction.

3. Results and discussion

By general rate equation method, the three parallel reaction pathways r_1, r_2 and r_3 and be combined as an equivalent single pathway. After attach the pseudo single pathway to the first reaction step, denote as r in Fig. 1, the multi-cycles reaction network can be transferred to a single cycle reaction network. The cyclic reaction rate r can be derived easily by the method we derived. The explicit form of four reaction pathways are listed as:

$$r = \frac{k_h[k_a(C_{TG}C_M - \frac{k_e}{k_d k_a}C_{DG}C_{BD_1}) + k_b(C_{DG}C_M - \frac{k_f}{k_d k_b}C_{MG}C_{BD_2}) + k_c(C_{MG}C_M - \frac{k_g}{k_d k_c}C_{Gly}C_{BD_3})]}{1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG} + k_d C_M + k_e C_{DG}C_{BD_1} + k_f C_{MG}C_{BD_2} + k_g C_{Gly}C_{BD_3}}$$

$$r_1 = \frac{[\frac{k_a}{k_d} C_{TG}(k_d C_M + k_e C_{DG} C_{BD_1} + k_f C_{MG} C_{BD_2} + k_g C_{Gly} C_{BD_3}) - \frac{k_e}{k_d} C_{DG} C_{BD_1}(1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG})]k_h}{1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG} + k_d C_M + k_e C_{DG} C_{BD_1} + k_f C_{MG} C_{BD_2} + k_g C_{Gly} C_{BD_3}}$$

$$r_2 = \frac{[\frac{k_b}{k_d} C_{DG}(k_d C_M + k_e C_{DG} C_{BD_1} + k_f C_{MG} C_{BD_2} + k_g C_{Gly} C_{BD_3}) - \frac{k_f}{k_d} C_{MG} C_{BD_2}(1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG})]k_h}{1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG} + k_d C_M + k_e C_{DG} C_{BD_1} + k_f C_{MG} C_{BD_2} + k_g C_{Gly} C_{BD_3}}$$

$$r_3 = \frac{[\frac{k_c}{k_d} C_{MG}(k_d C_M + k_e C_{DG} C_{BD_1} + k_f C_{MG} C_{BD_2} + k_g C_{Gly} C_{BD_3}) - \frac{k_g}{k_d} C_{Gly} C_{BD_3}(1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG}) C_{cat}]}{1 + k_a C_{TG} + k_b C_{DG} + k_c C_{MG} + k_d C_M + k_e C_{DG} C_{BD_1} + k_f C_{MG} C_{BD_2} + k_g C_{Gly} C_{BD_3}}$$

The reaction rate for each component can be expressed as, $r_{BD} = r$, $r_M = -r$, $r_{Gly} = r_3$, $r_{TG} = -r_1$, $r_{DG} = r_1 - r_2$, and $r_{MG} = r_2 - r_3$. There are eight lumped kinetic parameters k_a to k_h which are combined by rate constant of original eight reaction pathways. For example, $k_a = k_{12}/k_{10}$. All lumped kinetic parameters can be fit with experimental data by nonlinear regression.

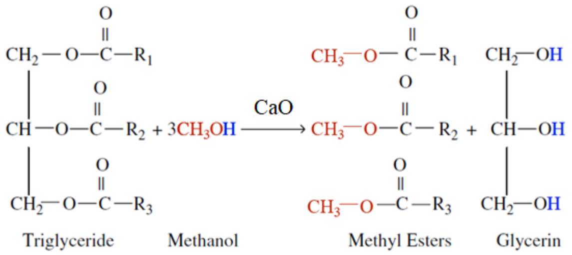

Figure 1. Transesterification of triglyceride with methanol by calcium oxide catalyst.

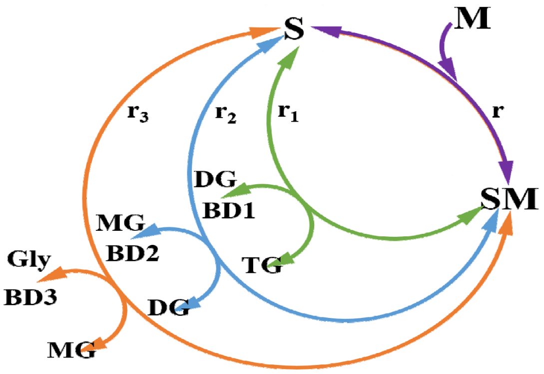

Figure 2. Proposed reaction network for triglyceride transesterification (TG: Triglyceride, DG: Diglyceride, MG: Monoglyceride, M: Methanol, BD1、BD2、BD3: Biodiesel, Gly: Glycerin, S: Free active site in catalyst, SM: Methanol-occupied site).

4. Conclusions

The kinetics of heterogeneous triglyceride transesterification with methanol by calcium oxide catalyst to produce biodiesel has been analyzed. A reasonable reaction network was proposed and the transesterification rate was derived. The experimental biodiesel yields using different catalyst doses and methanol to oil ratios were compared with model predictions and the results were satisfactory.

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