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Reaction conditions and kinetics for synthesizing methyl oleate

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ABSTRACT

Effects of different reaction conditions such as the amount of catalysts, the molar ratio of oleic acid to methanol, the reaction temperature, the retention time and the reaction time on the synthesis of methyl oleate have been discussed. Kinetics equations have also been applied on methyl oleate system. The results show that kinetic equations may predict the distribution of product and the experimental data are in agreement with the quantitatively analytical conclusions drawn from the calculated data.

KEYWORDS

Reaction condition;
Kinetics;
Synthesize;
Methyl oleate.

INTRODUCTION

Methyl oleate is one of the chemical products in the grease chemical industry. Methyl oleate as grease feedstock takes the place of fatty acid. It is also used as detergent, emulsifier, wetting agent and stabilizer of intermediates, etc. The usage of methyl oleate is gradually increased. Furthermore, methyl oleate as a pesticides and auxiliary agent quickly and effectively kills injurious insect. Methyl oleate as a biodiesel also takes the place of diesel and is one type of clean fuel[1]. Methanol, with concentrated sulphuric acid as a catalyst, reacts with oleic acid to synthesise methyl oleate. Concentrated sulphuric acid has a lot of disadvantages such as long reaction time, low yield and purity of methyl oleate. Large amount of waste water is discharged to cause the problem of environmental pollution and equipments are seriously corroded at the same time[2].

In the present paper, effects of different reaction conditions such as the amount of catalysts, the molar ratio of oleic acid to methanol, the reaction temperature, the retention time and the reaction time on the synthesis of methyl oleate have been discussed. Kinetics equations have also been pointed out.

RESULTS AND DISCUSSION

Effects of the amount of catalyst on yields of methyl oleate

Wang Jilin[3] studied effects of the amount of ionic liquid N-methyl-N-butyl morpholine hydroxide on yields of methyl oleate by keeping the molar ratio of oleic acid to methanol (1.0: 6.0), the reaction time (10 hour) and the reaction temperature (60 °C). The experimental results, TABLE 1, show that the yield of methyl oleate increased with an increase in the amount of ionic liquid N-methyl-N-butyl morpholine hydroxide. It was observed that the maximum yield of methyl oleate 95.1 % was attained when the amount of ionic liquid N-methyl-N-butyl morpholine hydroxide was 20 % of total reactant.

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TABLE 1 : Effects of the amount of catalyst on yields of methyl oleate

Amount of catalyst, %	Reaction time, h	Molar ratio of oleic acid to methanol	Yield of Methyl oleate, %
5	10	1.0:6.0	62.4
10	10	1.0:6.0	82.9
15	10	1.0:6.0	93.9
20	10	1.0:6.0	95.1

Effects of the molar ratio of oleic acid to methanol on yields of methyl oleate

Wang Jilin[3] used ionic liquid N-methyl-N-butyl morpholine hydroxide as a catalyst and oleic acid and methanol as feedstocks to synthesise methyl oleate. The reaction time and the amount of ionic liquid N-methyl-N-butyl morpholine hydroxide kept at constants were 10.0 hours and 15 % of total reactant, respectively. Effects of the molar ratio of oleic acid to methanol on yields of methyl oleate had been discussed. TABLE 2 showed effects of the molar ratio of oleic acid to methanol on yields of methyl oleate. The yield of methyl oleate increased with an increase in the molar ratio of oleic acid to methanol. When the molar ratio of oleic acid to methanol was 1.0 : 8.0, the maximum yield of methyl oleate attained was 96.3 %.

TABLE 2 : Effects of the molar ratio of oleic acid to methanol on yields of methyl oleate

Amount of catalyst, %	Reaction time, h	Molar ratio of oleic acid to methanol	Yield of Methyl oleate, %
15	10	1.0:1.0	57.5
15	10	1.0:2.0	59.8
15	10	1.0:4.0	71.7
15	10	1.0:8.0	95.2

Effects of the reaction temperature on yields of methyl oleate

Jiang Huiliang[4] replaced concentrated sulfuric acid with cation exchange resin as a catalyst to synthesise methyl oleate. The retention time and the molar ratio of oleic acid to methanol kept at constants were 40 minutes and 1.0 : 2.0, respectively. The effect of the reaction temperature on yields of methyl oleate had also been discussed. Figure 1 presented effects of the reaction temperature on yields of methyl oleate.

The yield of methyl oleate gradually increased with an increase in the reaction temperature. It was noticed that when the reaction temperature was 60 °C, the maximum yield of methyl oleate attained was 99.37 %.

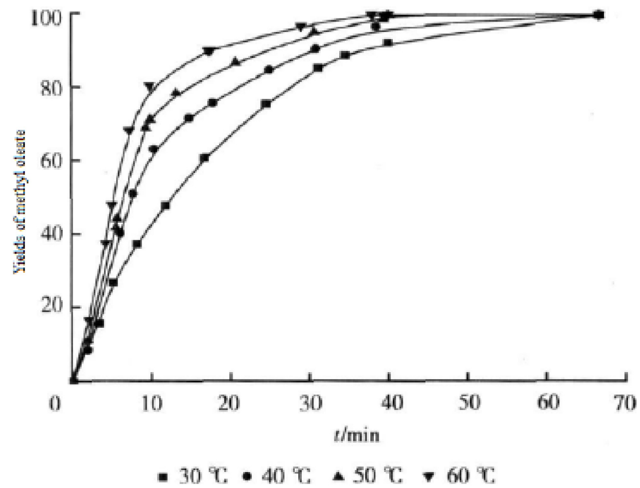

Figure 1 : Effects of the reaction temperature on yields of methyl oleate

Effects of the retention time on yields of methyl oleate

Jiang Huiliang[4] described effects of the retention time on yields of methyl oleate. When the molar ratio of oleic acid to methanol (1.0 : 2.0) and the reaction temperature (60°C) were kept constants. The experimental results presented in Figure 2 show that the yield of methyl oleate increased with an increase in the retention time. It was noticed that the maximum yield of methyl oleate above 99 % was attained when the retention time was 40 minutes.

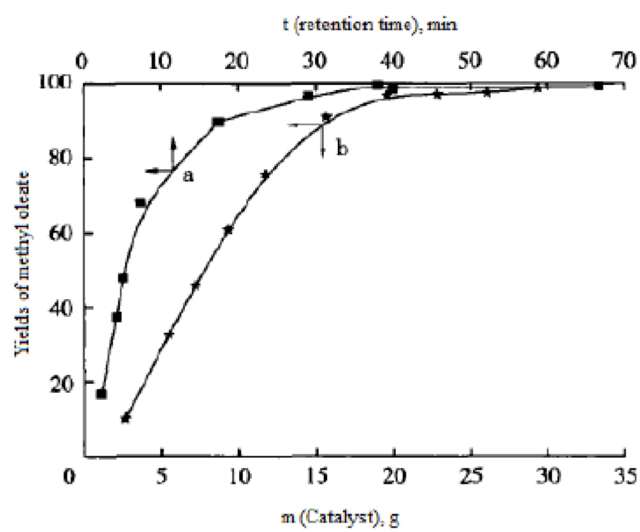

Figure 2 : Effects of the retention time on yields of methyl oleate

Effects of the reaction time on yields of methyl oleate

Liu Chusheng 1 used bismuth phosphotungstate as the catalyst while the molar ratio of oleic acid to methanol (1.0 : 1.4) and the amount of bismuth phosphotungstate (1.5 g). Effects of the reaction time, TABLE 3, indicated that the yield of increased with an increase in the reaction time. When the reaction time was 4 hours, the maximum yield of methyl oleate was 93.4 %. When the reaction time was more than 4 hours, the yield of methyl oleate did not increase.

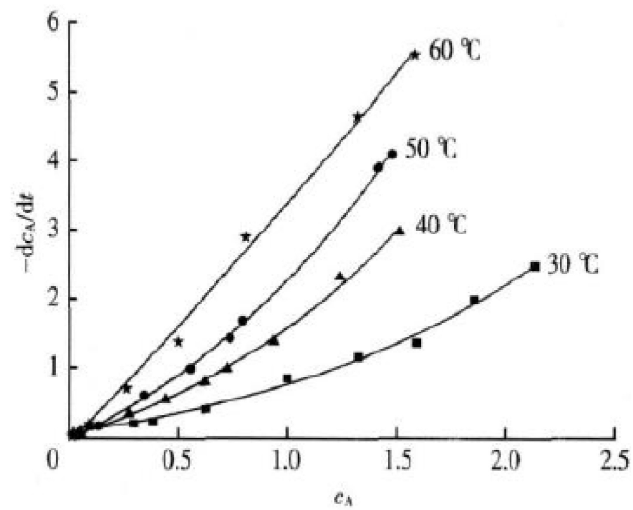

Figure 3 : Simulating curve at the different temperature

TABLE 3 : Effects of the reaction time on yields of methyl oleate

Reaction time, h	1	2	3	4	5
Yield of methyl oleate	48.2	70.5	87.6	93.4	93.4

KINETIC REACTION OF METHYL OLEATE

Foundation of kinetic models

Methyl oleate is produced when oleic acid reacts with methanol. Chemical reaction equation (1) of methyl oleate is described as follows:

$$C_{17}H_{33}COOH + CH_3OH \xrightarrow{Cation\ \ exchange\ \ resin} C_{17}H_{33}COOCH_3 + H_2O \quad \textbf{(1)}$$

J. Lilja[5] mentioned that in addition to diffusion control, generally, the catalytic reaction of cation exchange resin had the same reaction mechanism with the homogeneous catalytic reaction. Therefore, the authors used a homogeneous model to match the experimental data.

The reaction of fatty acids with alcohols is reversible reaction[6], which includes four basic reactions[5]. Furthermore, the reaction rate can be described as follows:

$$\mu = -\frac{1}{m}\frac{dc_A}{dt} = kc_A c_B - k' c_C c_D \quad \textbf{(2)}$$

$$k = (\frac{k_1 k_2}{k_{-1}}) \times c(H^+) \quad \textbf{(3)}$$

$$k' = (\frac{k_{-2} k_{-3} k_{-4}}{k_3 k_4}) \times c(H^+) \quad \textbf{(4)}$$

$$K = \frac{k}{k'} \quad \textbf{(5)}$$

$$K_{60°C} = 176.7258 \quad \textbf{(6)}$$

$$K_{50°C} = 162.3020 \quad \textbf{(7)}$$

$$K_{40°C} = 160.9501 \quad \textbf{(8)}$$

$$K_{30°C} = 139.8794 \quad \textbf{(9)}$$

Based on Equations (2) to (9), c_A, c_B, c_C and c_D are molar concentration of oleic acid, methanol, methyl oleate, and water, respectively; k and k' are velocity constant of the positive and reverse reaction separately; m is catalyst mass per volume; t is the reaction time; $k_1, k_2, k_3\ and\ k_4$ and $k_{-1}, k_{-2}, k_{-3}\ and\ k_{-4}$ are velocity constant of the positive and reverse reaction in the elementary reaction, respectively; $c(H^+)$ is H^+ concentration of resin phase dissociation; K is the equilibrium constant; $K_{60°C}$, $K_{50°C}$, $K_{40°C}$ and $K_{30°C}$ are the equilibrium constant at 60°C, 50°C, 40°C and 30°C, respectively.

Determination of kinetic model parameter

TABLE 4 shows the parameters of kinetics model. Concentration of oleic acid changes with the increase in the reaction time. Concentration of oleic acid in each set of experiments is plotted and calculated on the reaction time by using origin7.0. And then, the parameters of kinetics model can be obtained by using the least square method to match the experimental data.

Figure 3 shows the deviation between the experimental data and the curve fitting under the condition of the amount of catalyst (40 g) and molar ratio (2:1). Meanwhile, it indicates the experimental data fitting model, which proves the assumed reaction mechanism and kinetic model in the article are correct, and can describe the characteristics of the reaction accurately.

Determination of activation energy

According to the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad \textbf{(10)}$$

TABLE 4 : Parameters of kinetics model

T, °C	A	B
30	1.5758	0.0113
40	3.6988	0.0230
50	7.9090	0.0487
60	13.5372	0.0776

Note: A and B mean $k \times 10^3, L^2 \bullet mol^{-1} \bullet s^{-1} \bullet g^{-1}$ **and** $k' \times 10^3, L^2 \bullet mol^{-1} \bullet s^{-1} \bullet g^{-1}$**, respectively**

Figure 4 indicates the relationship between $\ln k$ and $\frac{1}{T}$, whereby the activation energy is written as follows:

$$E_a = 60.687 kJ / mol \quad \textbf{(11)}$$

$$k_{60°C} = 14.2856 \times 10^3 L^2 \bullet mol^{-1} \bullet s^{-1} \bullet g^{-1} \quad \textbf{(12)}$$

$$k_{50°C} = 7.1444 \times 10^3 L^2 \bullet mol^{-1} \bullet s^{-1} \bullet g^{-1} \quad \textbf{(13)}$$

$$k_{40°C} = 3.4222 \times 10^3 L^2 \bullet mol^{-1} \bullet s^{-1} \bullet g^{-1} \quad \textbf{(14)}$$

$$k_{30°C} = 1.5615 \times 10^3 L^2 \bullet mol^{-1} \bullet s^{-1} \bullet g^{-1} \quad \textbf{(15)}$$

The forums above is basic consistent with the velocity constant.

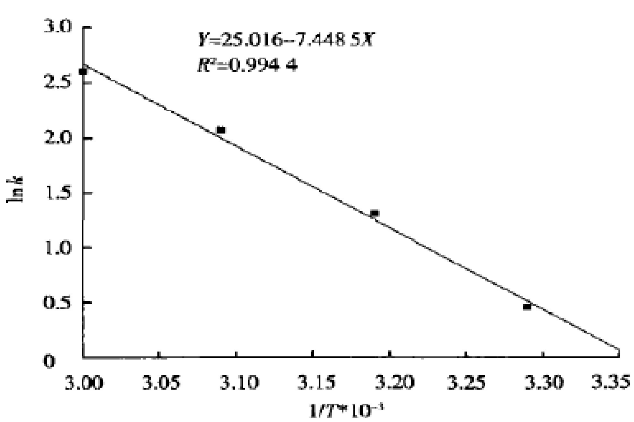

Figure 4 : Relationship between the reaction velocity constant and the reaction temperature

CONCLUSION

Effects of different reaction conditions such as the amount of catalysts, the molar ratio of oleic acid to methanol, the reaction temperature, the retention time and the reaction time were studied, and these are summarised as follows:

(1) The maximum yield of methyl oleate was 95.1 % under the condition of the amount of ionic liquid N-methyl-N-butyl morpholine hydroxide (20 % of total reactant).

(2) The maximum yield of methyl oleate was 96.3 % under the condition of the molar ratio of oleic acid to methanol (1.0 : 8.0).

(3) The maximum yield of methyl oleate was 99.37 % under the condition of the reaction temperature (60 °C).

(4) The maximum yield of methyl oleate was above 99 % under the condition of the retention time (40 minutes).

(5) The maximum yield of methyl oleate was above 93.4 % under the condition of the reaction time (4 hours).

(6) The experimental results showed that kinetic equations predicted the distribution of product and the experimental data were in agreement with the quantitatively analytical conclusions drawn from the calculated data.

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