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Synthetic methods and kinetics for synthesizing methyl oleate

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ABSTRACT

Nowadays a lot of synthetic methods of methyl oleate using different catalysts such as cation exchange resin, ionic liquids, mesoporous molecular sieve and bismuth phosphotungstate have been reviewed in the present paper. Yields of methyl oleate are improved by the addition of above catalysts. These methods are having the advantages of simple process and low investment costs. On the other hand, kinetic equations have been pointed out. The experimental 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

Synthetic methods;
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, different catalysts such as cation exchange resin, ionic liquids, mesoporous molecular sieve and bismuth phosphotungstate have been discussed. Kinetics equations have also been pointed out.

RESULTS AND DISCUSSION

Cation exchange resin as a catalyst to produce methyl oleate

Jiang Huiliang[3] introduced the preparation of methyl oleate and effects of the reaction conditions on its yield. The optimum conditions were the retention time (40 minutes), the reaction temperature (60 °C), the amount of cation exchange resin (20 g) and the molar ratio of oleic acid and methanol (1.0 : 2.0). The maximum yield of methyl oleate was 99.43%.

Ionic liquids as catalysts to generate methyl oleate

Wang Jinlin[4] described the synthetic method of ionic liquid N-methyl-N-butyl morpholine hydroxide and studied that the different conditions had also an ef-

fect on yields of methyl oleate. The experimental results indicated that the best conditions were that the reaction time, the molar ratio of oleic acid to methanol and the amount of ionic liquid N-methyl-N-butyl morpholine hydroxide were10 hours, 1.0 : 6.0 and 15 % of total reactant weight, respectively. The maximum yield of methyl oleate was 93.9 %.

Bo Yang[5] described the synthetic method of methyl oleate by using methyl pyridine acid ionic liquids as catalysts. Effects of the reaction conditions such as the reaction time, the reaction temperature, the molar ratio of oleic acid to methanol to methyl pyridine acid ionic liquids had been discussed. The best conditions were that the reaction time, the reaction temperature and the molar ratio of the molar ratio of oleic acid to methanol to methyl pyridine acid ionic liquids were 5 hours, 150 °C and 1.0:2.0:0.019, respectively. The maximum yield of methyl oleate was 88.21%.

Phosphotungstic acid/SiO_2 as catalysts to produce methyl oleate

Zhang Lixia[6] explained why modified phosphotungstic acid/SiO_2 as catalysts replaced concentrated sulfuric acid to synthesise methyl oleate. Effects of the reaction conditions such as the reaction time, the reaction temperature, the molar ratio of oleic acid to methanol and modified phosphotungstic acid/SiO_2's activation temperature had been discussed. The experimental results indicated that the best conditions were that the reaction time, the reaction temperature, the molar ratio of oleic acid to methanol and modified phosphotungstic acid/SiO_2's activation temperature were 8 hours, 80 °C, 1.0:8.0 and 180°C, respectively. The maximum yield of methyl oleate was 83.0%.

Mesoporous molecular sieve as a catalyst to generate methyl oleate

Sheng Jian[7] described the synthetic method of methyl oleate by using mesoporous molecular sieve SBA-15-SO_3H as a catalyst. Effects of the reaction conditions such as the amount of mesoporous molecular sieve SBA-15-SO_3H, the molar ratio of oleic acid to methanol and the reaction temperature had been discussed. The best conditions were that the amount of mesoporous molecular sieve SBA-15-SO_3H, the molar ratio of oleic acid to methanol and the reaction temperature were 42.86 % of total reactant, 1.0:2.0 and 60 °C, respectively. The maximum yield of methyl oleate was 72.0 %.

Cui Xiaoyan[8] used SBA-15/K_2O as a catalyst to generate methyl oleate. Effects of the reaction conditions such as the loading amount of K_2O, the molar ratio of oleic acid to methanol, the reaction temperature, the reaction time and the amount of SBA-15/K_2O had been discussed. The best conditions were that the loading amount of K_2O, the molar ratio of oleic acid to methanol, the reaction temperature, the reaction time and the amount of SBA-15/K_2O were 2 % of SBA-15, 1.0 :2.0, 180 °C, 4 hours and 5.0 % of total reactant, respectively. The maximum yield of methyl oleate was 83.61 %. After recovery and reuse of SBA-15/K_2O as a catalyst, it was noticed that its catalytic performance was very good.

Bismuth phosphotungstate as catalysts to produce methyl oleate

Liu Chusheng[1] studied the preparation of bismuth phosphotungstate and effects of the reaction conditions such as the amount of oleic acid, the molar ratio of oleic acid to methanol, the amount of bismuth phosphotungstate and the reaction time had been discussed. The best conditions were that the amount of oleic acid, the molar ratio of oleic acid to methanol, the amount of bismuth phosphotungstate and the reaction time were 0.1 mol, 1.0:1.4, 1.5 g and 4 hours, respectively. The maximum yield of methyl oleate was 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:

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

J. Lilja[9] 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[10], which includes four basic reactions [9]. Furthermore, the reaction rate can be described as fol-

lows:

$$\mu = -\frac{1}{m}\frac{dc_A}{dt} = kc_Ac_B - k^{'}c_Cc_D \quad (2)$$

$$k = (\frac{k_1k_2}{k_{-1}}) \times c(H^+) \quad (3)$$

$$k^{'} = (\frac{k_{-2}k_{-3}k_{-4}}{k_3k_4}) \times c(H^+) \quad (4)$$

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

$$K_{60°C} = 176.7258 \quad (6)$$

$$K_{50°C} = 162.3020 \quad (7)$$

$$K_{40°C} = 160.9501 \quad (8)$$

$$K_{30°C} = 139.8794 \quad (9)$$

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 1 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 1 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.

TABLE 1 : 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

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

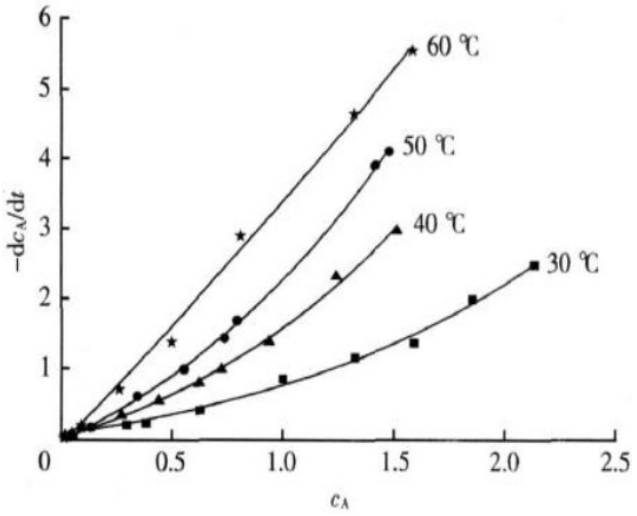

Figure 1: Simulating curve at the different temperature

Determination of activation energy

According to the Arrhenius equation:

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

Figure 2 indicates the relationship between $\ln k$ and $\frac{1}{T}$, whereby the activation energy is written as follows:

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

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

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

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

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

The forums above is basic consistent with the velocity constant.

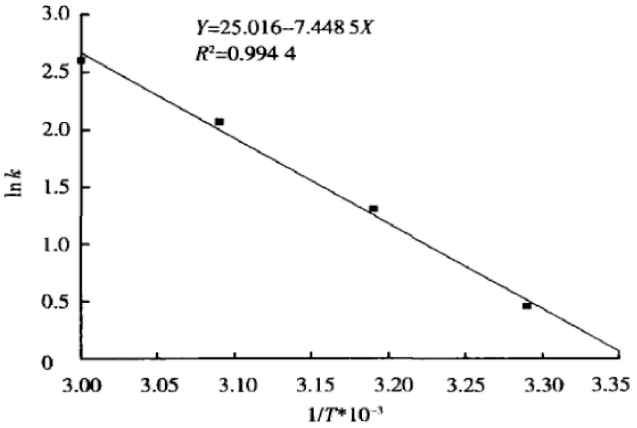

Figure 2 : Relationship between the reaction velocity constant and the reaction temperature

CONCLUSION

Based on the above discussion and review, cation exchange resin is found to be one of the best catalysts. It is used to produce the highest methyl oleate yield (99.43%). On the other hand, SBA-15-SO_3H is found to be one of the worst catalysts and its maximum yield of methyl oleate only reaches 72.0%. 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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