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Study on synthesis of methyl oleate catalyzed by ceric ammonium sulfate

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Abstract—Using oleic acid and methanol as the reactants and ammonium ceric sulfate as the catalyst, the synthesis of methyl oleate was studied. The influence of reaction conditions on esterification was investigated by orthogonal experimental design. The results showed that the conversion of 86.3% was attained under the optimum reaction condition as follows: reaction temperature 75℃, reaction time 4h, the molar ratio of methanol to oleic acid is 1.6, and the amount of catalyst is 6%(wt), it should be noted that the catalyst can be reused for 5 times without obvious loss of its activity.

Index Terms—Methyl oleate；Ammonium ceric sulfate；Catalytic；Esterification

1 Introduction

WITH the fossil fuels becoming depleted, coal, oil and natural gas prices continue to rise, the environmental pollution problems caused by fossil fuel combustion and vehicle exhaust emissions gradual deterioration, make human urgent need to find new, clean alternative energy [1]. Biodiesel (fatty acid methyl ester) become the generation products to petroleum products due to their biodegradable, renewable, clean and non-toxic, burning completely and many other advantages. At the same time, methyl oleate in the oleochemical industry occupies an important position, can replace fatty acid as a raw material of many oleochemicals, can be used as detergents, emulsifiers, wetting agents and intermediate stabilizer. Usage of methyl oleate is gradually increasing, be used as pesticide adjuvant can improve the penetration of pesticides, more quickly and effectively eradicate pests, role play the obvious synergism on insecticide. It is obtained by methanol and oleic acid role in the concentrated sulfuric acid after esterification, mainly in the industrial production. But there are many byproducts, equipment corrosion and serious environmental pollution problems. Since liquid acid and products are the same as the liquid phase, it will be very difficult to separate them completely, therefore people carried out a lot of improvements in the catalyst and production process, such as use solid acid[2], ionic liquids[3,4] and mesoporous molecular sieves[5,6] etc. instead of sulfuric acid, but there is not reports about ceric ammonium sulfate as catalyst for the synthesis of methyl oleate. The ceric ammonium sulfate was used as catalyst for the synthesis of methyl oleate in this study, the results show that its catalytic activity is excellent and the reusing ability of the catalyst is outstanding.

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2 Experimental

2.1 Experimental reagents and instrument

Oleic acid (AR, Tianjin HENG XING Chemical Reagent Co., Ltd.)； Methanol(AR, Tianjin GUANG FU Fine Chemical Plant); Ceric ammonium sulfate(AR, Beijing Chemical Reagent); Sodium hydroxide(AR, LIAONING XINXING Reagent Co., Ltd.); Ethanol(AR, LIAONING XINXING Reagent Co., Ltd).

DF-101S collector constant temperature heating magnetic stirrer(GONGYI YUHUA Instrument Co., Ltd.); AUY220 electronic balance(SHANG HUA GUANG ZHENG Medical Instrument Co., Ltd.); Magnetic stirrer(XIANG SU TAI XIAN Analytical Instrument Factory).

2.2 Esterification

Some amount of oleic acid, methanol and catalyst were put into a single necked flask with a reflux condenser in a thermostatic heating magnetic stirrer, after the reaction at needed conditions the reaction system was cooled to room temperature.

2.3 Determination of the rate of esterification reaction

The acid value before and after the reaction was determined based on GBT1668-2008. and the esterification conversion is calculated as follows:

$$\text{oleinic acid conversion\%} = \frac{\text{The initial acid of the reaction - The edd acid of reaction}}{\text{The initial acid of the reaction}} \times 100\% = \frac{V_0 - V_t}{V_0} \times 100\%$$

V_0, V_t – Volume of the NaOH-ethanol solution consumed for the reaction system before and after the reaction respectively.

3 Results and discussions

3.1 The conditions of orthogonal test reaction

Orthogonal experimental design method has the advantages of fewer number of experiments, representative, major factors can be identify in the intricacies of various factors, there are rules of analysis the impact of indicators of various factors. We

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therefore adopted orthogonal experimental design method, select $L_9(3^4)$ table, test each factor and horizontal are shown in Table 1, testing program and the results are shown in table 2.

TABLE 1
ORTHOGONAL LEVEL OF FORM FACTORS

Level	Factors			
	A	B	C	D
	Molar ratio	Reaction time h	Amount of catalyst %	Reaction temperature ℃
1	1.2	2	2	70
2	1.4	3	4	75
3	1.6	4	6	80

Note: the amount of catalyst = (mass of catalyst / mass of oleic acid)× 100%

TABLE 2
EXPERIMENTAL PROGRAM AND RESULTS OF ANALYSIS

NO.	Factors				Conversion %
	A	B	C	D	
1	1	1	1	1	29.87
2	1	2	2	2	36.67
3	1	3	3	3	78.00
4	2	1	2	3	43.33
5	2	2	3	1	24.00
6	2	3	1	2	86.21
7	3	1	3	2	71.52
8	3	2	1	3	82.91
9	3	3	2	1	55.33
R_1	59.29	48.24	66.33	36.40	
R_2	51.18	58.97	56.22	75.91	
R_3	69.92	73.18	57.84	68.08	
R	18.74	24.94	10.11	39.51	

Table 2 shows the influence extent order of each factor: D>B>A>C, and the optimal combination obtained by orthogonal experiment is $D_2B_3A_3C_1$, the optimal conditions reaction is temperature 75℃, reaction time 4h, molar ratio 1.6, 2% of the amount of catalyst in the esterification.

3.2 The affection of reaction temperature to the conversion

The impact of reaction temperature on the conversion of esterification is studied in fig.1 at such conditions: amount of catalyst 2%, reaction time 2.5h, molar ratio1.6.

It is seen from fig.1 that as the reaction temperature elevated, oleic acid conversion is increasing before 75℃ then declined slightly when the temperature is higher. This is because the esterification reaction is reversible, when the temperature is below 75℃, the reaction is kinetically controlled, elevated temperatures conducive to positive reaction direction, the conversion increased; When the temperature is higher than 75 ℃, reaction is controlled by thermodynamics, elevated temperature conducive to endothermic reverse reaction, the conversion is lower therefore the best reaction temperature is 75℃ .

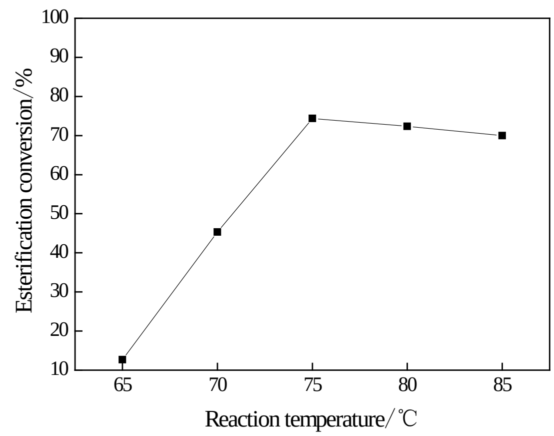

Fig. 1 The affection of reaction temperature to the conversion

3.3 The affection of the reaction time to the conversion

The impact of reaction time on the conversion of esterification is studied in fig.2 at such conditions: amount of catalyst 2%, reaction temperature 75℃, molar ratio1.6.

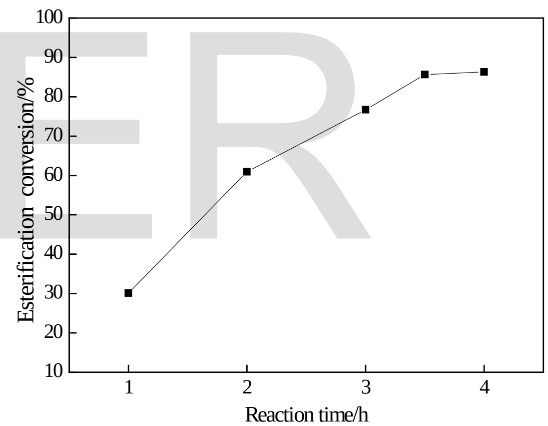

Fig. 2 The affection of reaction time to the conversion

It is seen from fig.2 that as the reaction time increased, oleic acid conversion increased gradually, but the conversion changes slowly when the reaction time is longer than 3.5 h, then the system has basically reached the equilibrium.

3.4 The affection of molar ratio to the conversion

The impact of molar ratio of the raw material on the conversion of esterification is studied in fig.3 at such conditions: amount of catalyst 2%, reaction temperature 75℃, reaction time 4 h.

It is seen from fig.3 that esterification of oleic acid is increased with molar ratio of the increase, When the molar ratio is 1.6, reaches a maximum, and then decreased. This is because as the mole ratio increases, relatively lower concentrations of oleic acid, the reaction rate is reduced, thus conversion declined, therefore the optimal molar ratio is 1.6.

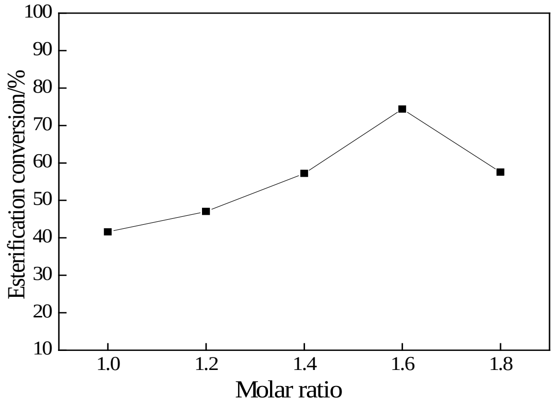

Fig. 3 The affection of molar ratio to the conversion

3.5 The affection of the amount of catalyst to the conversion

The impact of the amount of catalyst on the conversion of esterification is studied in fig.4 at such conditions: reaction temperature 75℃, molar ratio1.6, reaction time 4h.

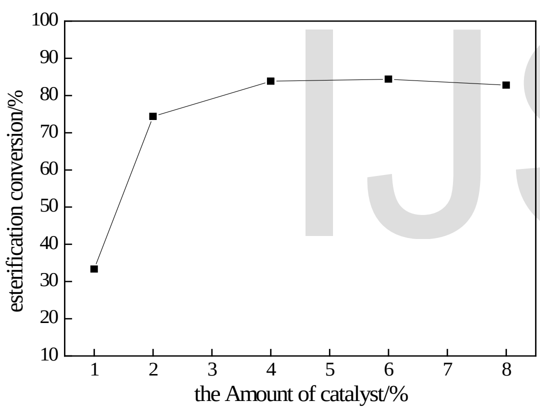

Fig. 4 The affection of the amount of catalyst to the conversion

It is seen from fig.4 with the increase of the catalyst amount, its conversion increases significantly. When the amount of ceric ammonium sulfate is 6%, its conversion reached 84.37%, however, further increase of catalyst amount, will not change the conversion significantly, so the amount of catalyst is selected as 6%.

3.6 The reusing ability of the catalyst

Reusing ability of the catalyst is studied under the optimal experimental conditions, the catalyst was collected by filtration after the reaction, then the catalyst is used for new reaction, every reaction result for each cycle of reaction was shown in fig.5.

It is shown in fig.5 that the catalyst's activity hasn't obvious decrease even after 5 cycles of reactions; therefore such catalyst's reusing ability is outstanding.

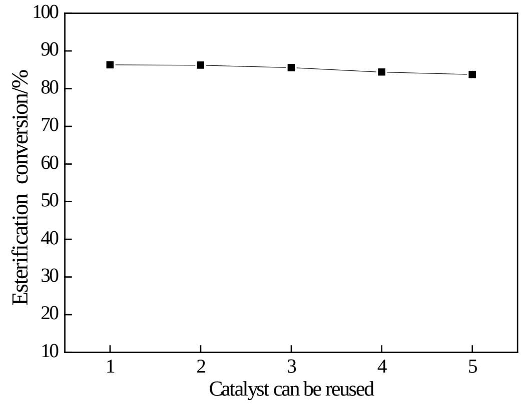

Fig. 5 The affection of catalyst can be reused to the conversion

4 Conclusions

Ceric ammonium sulfate has good catalytic activity and reusing ability in the reaction of oleic acid and methanol, the process is simple, and no pollution basically produces. The optimal reaction conditions are: the reaction temperature 75℃, reaction time 4h, molar ratio of 1.6, ceric ammonium sulfate catalyst dosage 6%(wt), at such conditions the conversion can reach 86.3%, and the catalytic performance has no significantly changes even after five times of reactions.

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