Study on synthesis of butyl oleate catalyzed by ceric ammonium sulfate

Xu Long, Li Jian, Yang Lina*, Sun Yumeng, Dong Jiali
(School of Petroleum and Chemical Technology, College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, China)

Abstract— Butyl oleate was synthesized using oleic acid and n-butanol as raw materials, ceric ammonium sulfate as catalyst. The influences of reaction conditions on esterification were investigated by orthogonal experimental design. The results showed that the conversion of 97.1% was attained under the optimum reaction condition as follows: reaction temperature 140 ℃, reaction time2.5 h, the molar ratio of n-butanol to oleic acid 2.5:1, and the amount of catalyst 5%(wt), the esterification conversion can still reach 60.1% after four times of repeated uses.

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

1 INTRODUCTION

BUTYL oleate (n-butyl oblate) is a kind of long-chain fatty acid ester with carbon-carbon unsaturated double bond. It has good performances in such applications such as plasticizer, lubricating oil additives, wetting agent and industrial solvents etc. Traditional butyl oleate synthesis method starts from oleic acid and n-butanol using concentrated sulfuric acid as catalyst [. High catalytic activity and low cost make it favorable in the esterification, but the following disadvantages[1,2]: (1) under the esterification reaction conditions, both concentrated sulfuric esterification, dehydration and oxidation, accompanied by side reactions, reaction product containing a small amount of ether, sulfuric acid ester, unsaturated compounds and carbonyl compounds, to the product purification and recovery difficult; (2) concentrated sulfuric acid as a catalyst subject to alkali neutralization, washing, post-treatment process complex, reaction products and unreacted raw material loss, accompanied by a large number of waste generated, easy to cause environmental pollution; (3) the reaction of concentrated sulfuric acid corrosion of equipment seriously. In recent years, there have been reports in solid superacid [3,4], heteropoly acids [5,6], biological enzyme [7,8] as the catalyst for synthesis of butyl oleate, but there is not reports about ceric ammonium sulfate as catalyst for the synthesis of butyl 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.

2 EXPERIMENTAL

2.1 Experimental reagents and instrument

Oleic acid(AR, Tianjin Hengxing Chemical Reagent Co., Ltd.); N-butanol(AR, Shenyang Sinopharm Chemical Reagent Co., Ltd.); 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 therefore adopted orthogonal experimental design method, select L_9 (3^4) table, test each factor and horizontal are shown in

- *Xu Long postgraduate students engaged in the production of clean fuels in Liaoning Shihua University, China. E-mail: xulongliaogong@126.com*
- *Professor Yang Lina* engaged in the production of clean fuesl in Liaoning Shihua University, China. E-mail: lnqdsd@yahoo.com.cn*

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
	Reaction temperature ℃	Reaction time h	Molar ratio	Amount of catalyst %
1	120	1.5	2	2
2	130	2.5	1	4
3	140	3.5	0.5	6

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

TABLE 2
EXPERIMENTAL PROGRAM AND RESULTS OF ANALYSIS

NO.	Factors				conversion /%
	A	B	C	D	
1	1	1	1	1	9.5
2	1	2	2	2	11.2
3	1	3	3	3	31.2
4	2	1	2	3	37.1
5	2	2	3	1	56.1
6	2	3	1	2	85.6
7	3	1	3	2	39.8
8	3	2	1	3	95.8
9	3	3	2	1	62.4
R_1	17.300	28.800	63.633	42.667	
R_2	59.600	54.367	36.900	45.533	
R_3	66.000	59.733	42.367	54.700	
R	48.700	30.933	26.733	12.033	

Table 2 shows the influence extent order of each factor: A>B>C>D, and the optimal combination obtained by orthogonal experiment is $A_3B_3C_1D_3$, the optimal conditions reaction is temperature 140℃, reaction time 3.5 h, molar ratio 2, 6% 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 3%, reaction time 2.5 h, molar ratio 2.

It is seen from fig.1 that as the reaction temperature elevated, oleic acid conversion is increasing before140℃ then declined slightly when the temperature is higher. This is because the esterification reaction is reversible, when the temperature is below 140℃, the reaction is kinetically controlled, elevated temperatures conducive to positive reaction direction, the conversion increased; When the temperature is higher than 140℃, reaction is controlled by thermodynamics, elevated temperature conducive to endothermic reverse reaction, the conversion basically unchanged and side reactions may increase, therefore the best reaction temperature is 140℃, at this point esterification conversion was 93.2%.

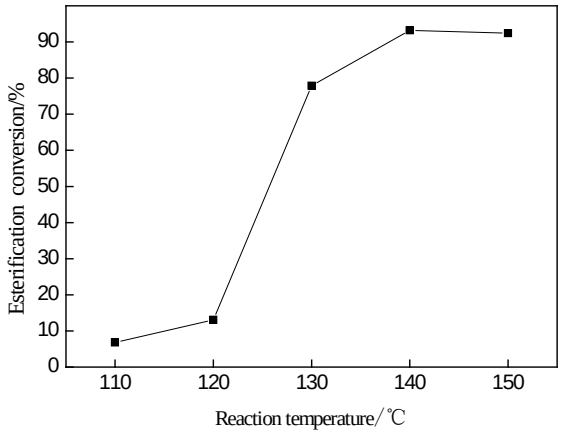

Fig.1 The affection of reaction temperature to the conversion

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 3%, reaction temperature 140℃, molar ratio 2(butanol 0.03 mol).

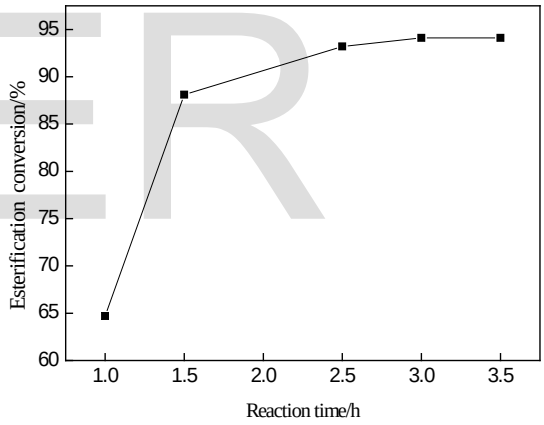

Fig. 2 The affection of reaction time to the conversion

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 h, then the system has basically reached the equilibrium. Therefore, to determine the optimum reaction time 3 h, the esterification rate was 94.1% at this time.

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 3%, reaction temperature 140℃, reaction time 3 h, oleic acid 0.015 mol.

It is seen from fig.3 that esterification of oleic acid is increased with molar ratio of the increase, When the molar ratio is 2.5, 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 2.5.

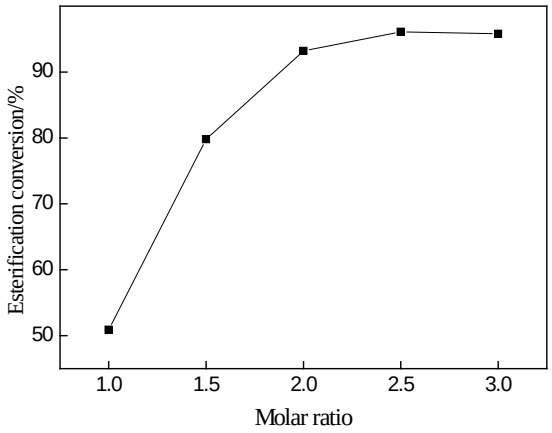

Fig. 3 The affection of molar ratio to the conversion

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 140℃, molar ratio 2.5 (n-butanol 0.03 mol), reaction time 3 h.

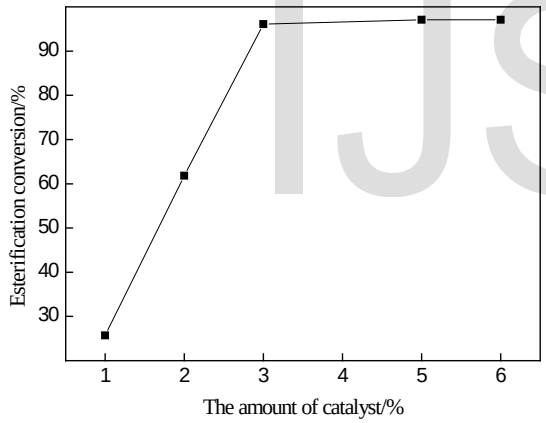

Fig. 4 The affection of the amount of catalyst to the conversion

It is seen from fig.4 that when the amount of the catalyst is less than 3%, with the increase of the catalyst amount, its conversion increases significantly. With the increase in volume of catalyst, the rate of synthesis of butyl oleate accelerated, reducing the time used for the reaction, so that the synthesis of butyl oleate esterification rate increased, when the amount of ceric ammonium sulfate is more than 3%, further increase of catalyst amount, will not change the conversion significantly. When the amount of ceric ammonium sulfate is 5%, its conversion reached the maximum of 97.1%, Therefore, to determine the optimum amount of catalyst is 5%, then the esterification rate was 97.1%.

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 table 3.

TABLE 3
THE AFFECTION OF THE REUSING ABILITY OF CATALYST TO THE CONVERSION

The reusing ability of catalyst	1	2	3	4	5
Conversion（%）	97.1	91.8	82.4	73.9	60.1

It can be seen from Table 3, along with increase the frequency of use catalyst, esterification catalyst capacity decreased, but still after five times, esterification rate can reach 60.1%, therefore, the catalyst is stability.

4 CONCLUSIONS

Ceric ammonium sulfate has good catalytic activity and reusing ability in the reaction of oleic acid and n-butanol, the process is simple, and no pollution basically produces. The optimal reaction conditions are: the reaction temperature 140℃, reaction time 3h, molar ratio of 2.5, ceric ammonium sulfate catalyst dosage 5%(wt), at such conditions the conversion can reach 97.1%, and the catalytic performance has no significantly changes even after five times of reactions.

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