



## Catalytic Synthesis of the Iso-octyl Palmitate from Palmitic Acid and Isooctanol with Water-Tolerant Solid Acid

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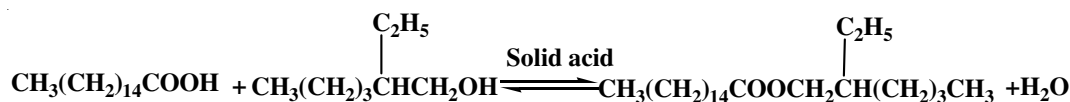
Iso-octyl palmitate is synthesized *via* esterification of palmitic acid and isooctanol when the water-tolerant solid acid is used as the catalyst. The particular chelate molecular structure of  $\text{SnC}_2\text{O}_4$  makes Sn atom have the suitable acid intensity. The steric hindrance in the course of the reaction is reduced because of its molecular structure with the plane surface. In addition, the stability of molecule of  $\text{SnC}_2\text{O}_4$  is strengthened because of its chelate molecular structure. All these factors lead to its high catalytic activity in the esterification reaction. Many factors, which have an effect on the yield of iso-octyl palmitate, have been studied. The reaction conditions for synthesizing iso-octyl palmitate with high yield are optimized with the orthogonal experiment. The optimum conditions for synthesizing iso-octyl palmitate with high yield are as follows: reaction time is 2.5 h and the mol ratio of isooctanol to palmitic acid is 1.8:1 and the dosage of the catalyst is 2.0 % and the reaction temperature is 150 °C.

**Key Words:** Catalytic synthesis, Iso-octyl palmitate, Water-tolerant solid acid, Orthogonal experiment.

### INTRODUCTION

Iso-octyl palmitate (IOP) is a kind of non-ionic surfactant, has been widely used in cosmetics, synthetic lubricants, textile industries and oil industries<sup>1-4</sup>. Recently iso-octyl palmitate has attracted much attention as plasticizer in the field of plastics industry. At present, iso-octyl palmitate has commercially been synthesized from palmitic acid and isooctanol using strong liquid acid such as  $\text{H}_2\text{SO}_4$ , sulfamic acid and toluene-*p*-sulfonic acid as the catalyst, but this process is not desirable because of many side reactions, which is caused by the strong oxidizing property of the liquid acid. This process is not environmentally benign because of the production of a large amount of waste acid and the disposal problem of the catalyst. Furthermore, the equipment is corroded severely by the liquid acid. In recent years, there have been some reports about the esterification of palmitic acid with isooctanol over enzymes such as immobilized lipase<sup>5-7</sup>. However, the activity of enzyme catalysts was not sufficient, thus causing the reaction time was excessively long.

It is keenly desirable to develop solid acids, which are effective for this reaction, since solid acids have several advantages, such as reusability, insolubility and ease of separation<sup>8</sup>. Furthermore, the corrosion of the equipment can be alleviated greatly through using the solid acids as the catalyst. Therefore, the use of solid acid instead of liquid acid is favourable economically, since the service life of equipment is prolonged. There are some papers concerning the esterification of polyatomic alcohol and polybasic carboxylic acid, which  $\text{SnC}_2\text{O}_4$  is used as the catalyst<sup>9,10</sup>. However, in the preparation of iso-octyl palmitate,  $\text{SnC}_2\text{O}_4$  used as catalyst has not been reported. In the present study, we wish to report that a solid acid catalyst,  $\text{SnC}_2\text{O}_4$ , is efficient for synthesis of iso-octyl palmitate from palmitic acid and isooctanol as shown in **Scheme-I**. This reaction system using a solid acid is recognized as an example of "green-sustainable chemistry". Factors, which have an influence on the yield of iso-octyl palmitate, have been investigated. The reaction conditions for synthesizing iso-octyl palmitate with high yield are optimized with the orthogonal experiment.



**Scheme-I:** Synthesis of IOP from palmitic acid and isooctanol using solid acid as catalyst

## EXPERIMENTAL

Palmitic acid, which is chemically pure grade, is obtained from Shanghai Chemical Reagents Supply Procurement of Five Chemical Plants. Isooctanol, which is analytically pure grade, is also obtained from Shanghai Chemical Reagents Supply Procurement of Five Chemical Plants. Cyclohexane, which is analytically pure grade, is purchased from Anhui Ante Biochemical Co. Ltd.  $\text{SnC}_2\text{O}_4$ , which is chemically pure grade, is supplied with Aladdin Reagent Company.  $\text{N}_2$ , which is stored in the steel cylinder, is purchased from Hangzhou Chemical Plant.

### Synthesis of iso-octyl palmitate

**Esterification of palmitic acid:** All the palmitic acid and part of isooctanol were introduced into a glass autoclave 100 mL in volume, which was equipped with the mechanical stirrer, reflux condenser and dropping funnel. Nitrogen was inlet into the glass autoclave to expel the air. Then the cyclohexane was added into the water knockout vessel. The glass autoclave was heated with the oil bath. The suspension was vigorously stirred with a mechanical stirrer and heated at the normal atmosphere after the palmitic acid was melted completely and  $\text{SnC}_2\text{O}_4$  was added into the glass autoclave. The rest of isooctanol was dripped into the glass autoclave slowly and uniformly when the produced water was extracted from the water knockout vessel. The reaction did not stop until no water entered the water knockout vessel. Thus, the crude iso-octyl palmitate was obtained.

**Separation of the catalyst and purification of the crude iso-octyl palmitate:** The catalyst was separated *via* filtering the crude iso-octyl palmitate. The filtrate was neutralized to neutrality with the solution of  $\text{Na}_2\text{CO}_3$ . The filtrate was washed with distilled water repeatedly. The upper organic phase was stratified and obtained with the separating funnel. The obtained organic phase was distilled under reduced pressure to separate the excess isooctanol, redundant cyclohexane, water and the side-products. Then it was cooled to the room temperature. The sample was tested and characterized with Fourier transform infrared spectrometer (FTIR) and gas chromatography.

## RESULTS AND DISCUSSION

**Reaction mechanism:** The particular chelate molecular structure of  $\text{SnC}_2\text{O}_4$  leads to its high catalytic activity.  $\text{SnC}_2\text{O}_4$  has the suitable acid intensity<sup>11</sup>. In the molecule of  $\text{SnC}_2\text{O}_4$ , every Sn atom presents stronger electrophilicity because it is influenced with strong electrophilic induction effect of four oxygen atoms, which are linked with Sn atom. Lewis acid intensity of Sn atom in the active centers can be improved. Therefore, oxygen atom of carboxyl in the molecule of palmitic acid is easier to coordinate with Sn atom. Thus the reaction velocity is accelerated. The steric hindrance in the course of the reaction is reduced because of its molecular structure with the plane surface. The lower steric hindrance of  $\text{SnC}_2\text{O}_4$  is beneficial to coordinate between oxygen atom of carboxyl and Sn atom. In addition, the molecule of  $\text{SnC}_2\text{O}_4$  has higher thermal stability, which is helpful to keep the catalytic activity of  $\text{SnC}_2\text{O}_4$  in the esterification reaction<sup>12</sup>. The plausible reaction mechanism is given in **Scheme-II**.

**Influence of the mol ratio of isooctanol to palmitic acid on the esterification reaction:** Fig. 1 shows that the yield of iso-octyl palmitate is increased with the increase of the mol ratio of isooctanol to palmitic acid. This can be explained by the fact that the esterification reaction of the palmitic acid with isooctanol is reversible reaction. The increase of the isooctanol is beneficial to produce more iso-octyl palmitate, thus causing higher yield of iso-octyl palmitate. In addition, the isooctanol acts as not only the reactant but also the solvent. Therefore, the practical mol ratio of isooctanol to palmitic acid is more than 1.0. However, Fig. 1 also shows that the yield of iso-octyl palmitate is decreased with the increase of the mol ratio of isooctanol to palmitic acid when the mol ratio of isooctanol to palmitic acid is more than 1.6. This is caused by the fact that the contents of palmitic acid and catalyst are decreased with the increase of the isooctanol. The content of the isooctanol, which actually participates in the esterification reaction, is also decreased because the excess isooctanol functions as the solvent. In view of the reaction equilibrium, the esterification reaction is shifted to the direction of the reverse reaction because of the decrease of the contents of the reactants. Thus, the yield of iso-octyl palmitate is decreased. Furthermore, the excess isooctanol can lead to more side reactions and increase the difficulty of purification of iso-octyl palmitate.

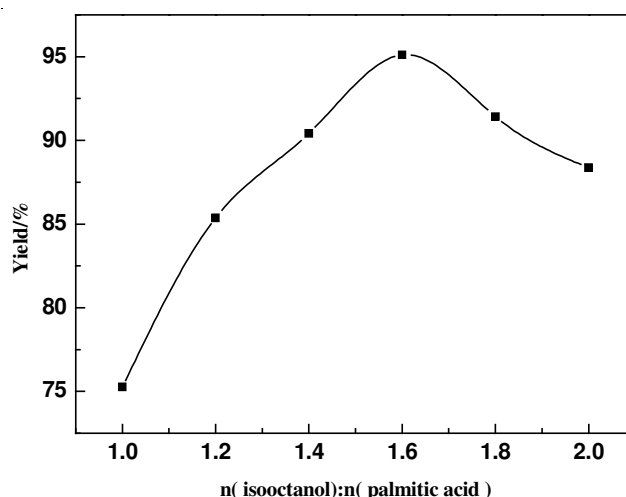
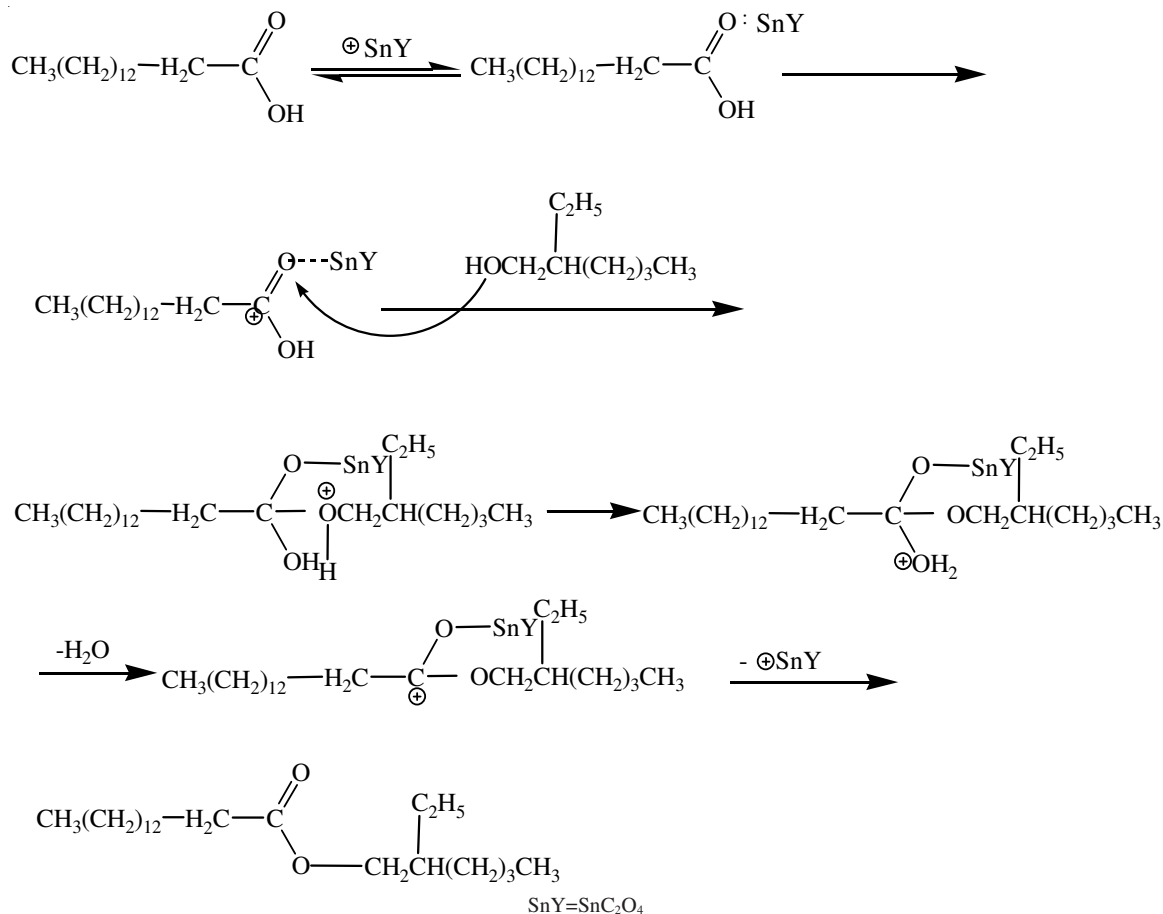


Fig. 1. Influence of the mol ratio of isooctanol to palmitic acid on the yield of iso-octyl palmitate

**Effect of the reaction time on the esterification reaction:** Fig. 2 shows that the yield of iso-octyl palmitate is very low when the reaction time is short. The reaction time is so short that the reaction can not be completed. Thus, the yield of iso-octyl palmitate is very low. Fig. 2 also shows the yield of iso-octyl palmitate can be increased *via* prolonging the reaction time. However, the yield of iso-octyl palmitate is decreased when the reaction is more than 3.5 h. It is known that the esterification reaction is the reversible reaction and the yield of iso-octyl palmitate is not increased any longer *via* prolonging the reaction time when the reaction equilibrium is reached. More side reactions are generated after the reaction equilibrium when the reaction time is prolonged again. Therefore, the yield of iso-octyl palmitate is decreased.



Scheme-II: Plausible reaction mechanism

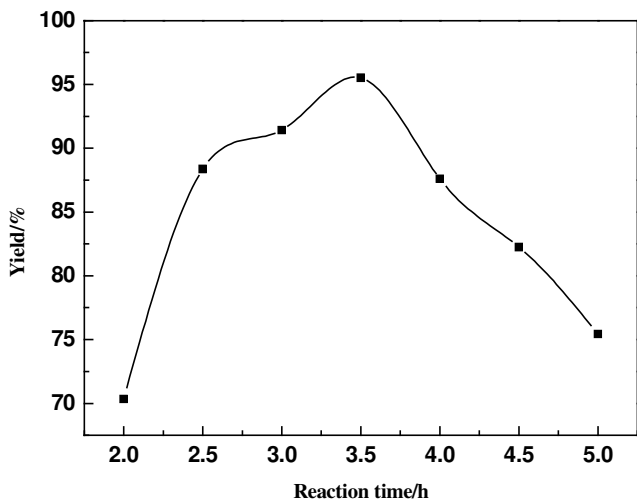


Fig. 2. Effect of the reaction time on the yielded of iso-octyl palmitate

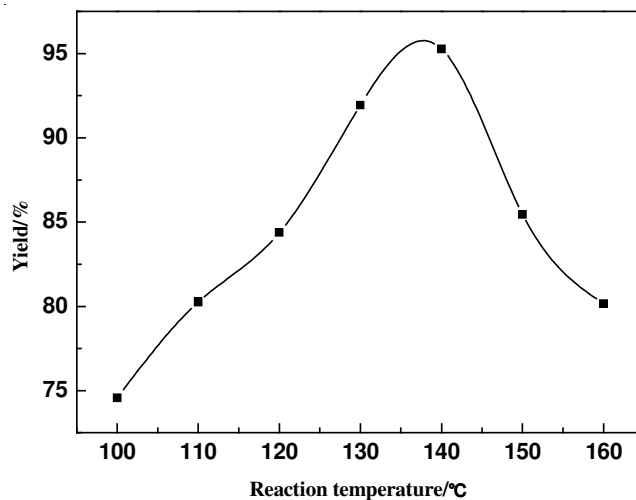


Fig. 3. Influence of the reaction temperature on the esterification reaction

**Influence of the reaction temperature on the esterification reaction:** Fig. 3 shows that the yield of iso-octyl palmitate is increased with the increase of the reaction temperature when the reaction temperature is lower than 140 °C. Usually, the esterification reaction is the endothermic reaction. The reaction rate of esterification is accelerated and the time of reaching the equilibrium is shortened, which is beneficial to improve the yield of iso-octyl palmitate when the reaction temperature is increased. In addition, the rate of backflow water-separating is raised, which accelerates the reaction further. However, Fig. 3

also shows that the yield of iso-octyl palmitate is decreased with the increase of the reaction temperature when the reaction temperature is more than 140 °C. This is caused by the fact that the higher reaction temperature can lead to more side reactions such as the dehydration reaction of the isooctanol and the decarboxylation reaction of the palmitic acid.

**Effect of the added amount of the entrainer on the esterification reaction:** Fig. 4 shows that the yield of iso-octyl palmitate is increased when the moderate amount of the entrainer is introduced into the reaction system. This can be

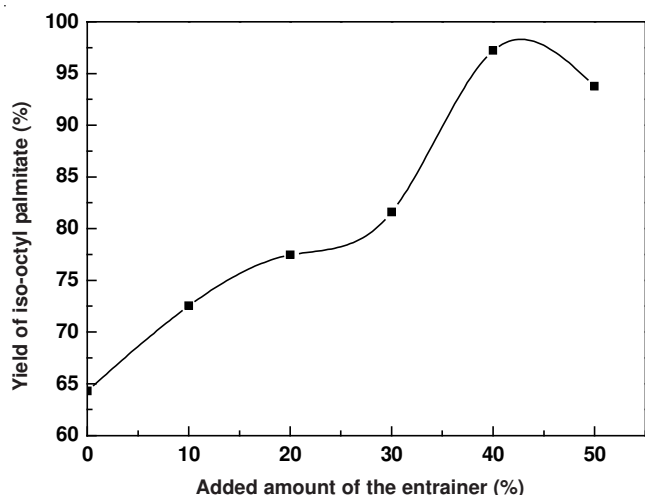


Fig. 4. Effect of the added amount of the entrainer on the esterification reaction

explained from the view of chemical thermodynamics and chemical kinetics. According to the theory of the chemical thermodynamics, the water is taken out of the reaction system in time when the azeotrope is formed *via* combining the entrainer and water. Thus, the thermodynamic equilibrium of the reaction is broken, which makes the reaction shift to the right, *i.e.*, more product can be obtained. According to the theory of the chemical kinetics, the water is taken out of the reaction system in time, *i.e.*, the content of water in the reaction system is decreased, which make the concentration of the reactants be increased, thus accelerating the reaction velocity. In addition, the reaction temperature can be reduced *via* adding the entrainer, which can suppress the side reactions. Therefore the yield of iso-octyl palmitate can be improved.

**Influence of the added amount of the catalyst on the esterification reaction:** Fig. 5 shows that the yield of iso-octyl palmitate is increased with the increase of the added amount of the catalyst when its dosage is lower than 2.5 %. The catalytic result is poor because there is no adequate active center when the dosage of the catalyst is small. In addition, the effective contact surface area between the reactants and the catalyst is small, thus causing the rate of esterification to decrease. The esterification does not reach the equilibrium within the fixed time. The effective contact surface area between the reactants and the catalyst is increased with the increase of the added amount of the catalyst. Thus, the rate of esterification is accelerated. However, Fig. 5 also shows that the yield of iso-octyl palmitate is decreased with the increase of the added amount of the catalyst when its dosage is more than 2.5 %. This phenomenon can be explained by the fact that excess catalyst leads to more side reactions.

**Orthogonal experiment for optimizing reaction conditions:** The orthogonal experiment table with four factors and three levels is designed to optimize reaction conditions. Orthogonal experiment result for optimizing reaction conditions is shown in Table-1. Table-1 shows that factors influencing the yield of iso-octyl palmitate in major and minor order is B > C > A > D. The better level is A2B2C2D3. The optimum conditions for synthesizing iso-octyl palmitate with high yield are as follows: reaction time is 2.5 h and the mol ratio of

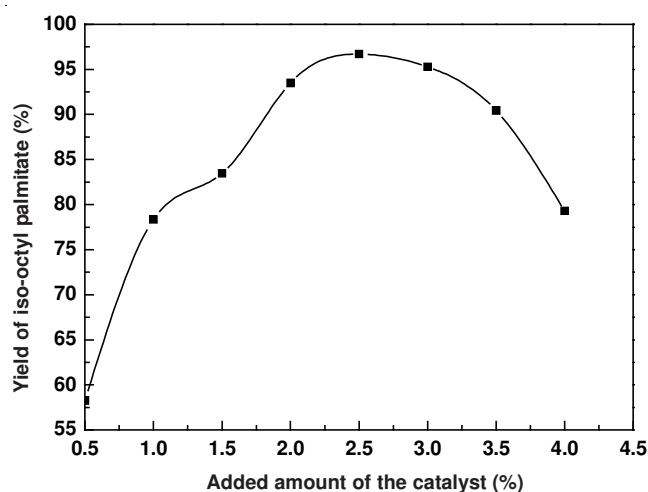


Fig. 5. Influence of the added amount of the catalyst on the esterification reaction

TABLE-1  
ORTHOGONAL EXPERIMENT RESULT FOR  
OPTIMIZING REACTION CONDITIONS

Entry	Factors and levels				Yield of IOP (%)
	A (h)	B	C (%)	D (°C)	
1	2.5	1.6:1	1.5	130	75.30
2	2.5	1.8:1	2.0	140	94.87
3	2.5	2.0:1	3.0	150	93.29
4	3.0	1.6:1	2.0	150	91.06
5	3.0	1.8:1	3.0	130	91.91
6	3.0	2.0:1	1.5	140	91.32
7	4.0	1.6:1	3.0	140	80.43
8	4.0	1.8:1	1.5	150	88.27
9	4.0	2.0:1	2.0	130	88.74
$k_1/3$	88.15	82.60	85.30	85.65	–
$k_2/3$	91.43	91.68	91.56	88.87	–
$k_3/3$	85.81	91.12	88.54	90.87	–
R	5.62	9.08	6.26	5.22	–

A: Reaction time; B:  $n(\text{isooctanol}) : n(\text{palmitic acid})$ ; C: Dosage of the catalyst; D: Reaction temperature.

isooctanol to palmitic acid is 1.8:1 and the dosage of the catalyst is 2.0 % and the reaction temperature is 150 °C. The repeated experiments under the optimum conditions are carried out. The yield of iso-octyl palmitate is 95.21 %.

**FTIR of iso-octyl palmitate:** FTIR of iso-octyl palmitate is shown in Fig. 6. 2957 $\text{cm}^{-1}$  is the characteristic stretching peak of  $-\text{CH}_3$ ; 2922 and 2853  $\text{cm}^{-1}$  are the stretching vibration peak of  $-\text{CH}_2-$ ; 1738  $\text{cm}^{-1}$  is the characteristic stretching peak of  $-\text{COO}^-$  and 1463  $\text{cm}^{-1}$  is the stretching vibration peak of  $\text{C}=\text{O}$ ; 1172  $\text{cm}^{-1}$  is the stretching vibration peak of  $-\text{C}-\text{O}-$  in the fatty acid ester with long chains. In Fig. 6, the characteristic stretching peak of  $-\text{OH}$  can not be found. Fig. 6 verifies clearly that iso-octyl palmitate has been synthesized successfully.

## Conclusion

The particular chelate molecular structure of  $\text{SnC}_2\text{O}_4$  makes Sn atom have the suitable acid intensity. The steric hindrance in the course of the reaction is reduced because of its molecular structure with the plane surface. In addition, the stability of molecule of  $\text{SnC}_2\text{O}_4$  is strengthened because of its chelate molecular structure. All the above factors lead to its high catalytic activity in the esterification reaction. Many

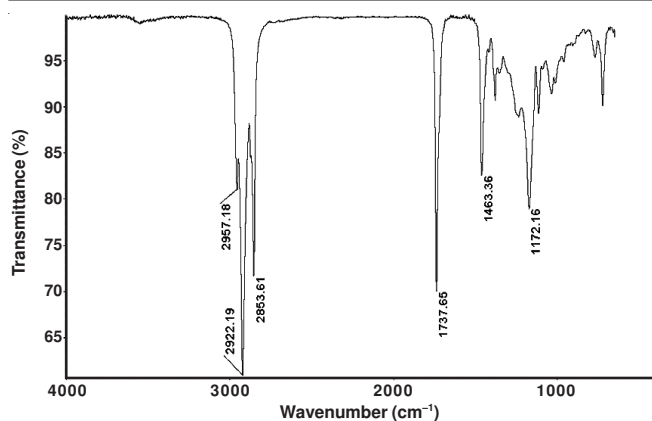


Fig. 6. FTIR of iso-octyl palmitate

factors, such as the mol ratio of isooctanol to palmitic acid, the reaction time, the reaction temperature and the added amounts of the entrainer and the catalyst have an influence on the yield of iso-octyl palmitate. The optimum conditions for synthesizing iso-octyl palmitate with high yield are as follows:

reaction time is 2.5 h and the mol ratio of isooctanol to palmitic acid is 1.8:1 and the dosage of the catalyst is 2.0 % and the reaction temperature is 150 °C.

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