Chen Keke, Du Huan, Zhang Jiawen, Zhang Xiaofang, Kuang Yingying and Han Xiaoxiang*

Catalytic synthesis of methyl caprylate using multi-SO_3H functionalized Brønsted acidic ionic liquid as catalyst

Abstract: Environmentally benign Brønsted acidic ionic liquids with multi-SO_3H functionality were prepared using N-methyl imidazole and 1,3-propane sultone as the source chemicals. The prepared ionic liquid catalysts were characterized by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and thermogravimetry (TG) and their catalytic activity in esterification of caprylic acid with methanol was investigated. The results showed that the novel catalyst was very efficient for the reaction, with excellent water and acid resistant ability. Under optimum conditions, the yield of methyl caprylate reached 94.8%. The ionic liquids could be reused six times without a noticeable drop in activity. The kinetic study for the esterification indicated that the reaction order was 1.54 and the activation energy E_a was 24.61 kJ/mol.

Keywords: esterification; ionic liquid; methyl caprylate.

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1 Introduction

Esters have been used extensively in chemical industries as important intermediates, and also as important components of many spices [1]. A number of approaches for the esterification of carboxylic acids and alcohols have been introduced. The esterification in industry was traditionally carried out by mineral acids, such as H_2SO_4, HF and H_3PO_4, mainly on account of high catalytic activity and low prices. It is well known that these catalysts have attracted much attention for their inherent problems of corrosiveness, more byproducts, environmental problems and difficulty in catalyst recovery and reuse. To overcome these disadvantages, efforts have been made in the development of heterogeneous catalysts systems. Supported mineral acid [2], resins [3], zeolites [4] by different groups and heteropoly acids [5] have shown a high activity on the esterification of carboxylic acids. However, all these processes and catalysts have one or more problems related to product selectivity, environmental safety, spent catalyst disposal and catalyst recyclability.

Recently, ionic liquids as solvents or catalysts have attracted an increasing interest in organic reactions [6–8]. As environmentally friendly solvents or catalysts, ionic liquids are relatively perfect with respect to the principles of green chemistry and have been investigated widely due to their advantageous properties [6, 7, 9], such as negligible vapor pressure, excellent chemical and thermal stability, potential recoverability and recyclability [10–14]. Ionic liquids, especially Brønsted acidic ionic liquid, showed high catalytic activity on the esterification [15, 16]. In this work, we prepared a strong Brønsted acidic ionic liquid with four -SO_3H groups and studied the catalytic activities of the obtained catalysts through the esterification reactions of caprylic acid with methanol. The kinetic model for the esterification was also established and evaluated under optimized conditions.

2 Materials and methods

2.1 Catalyst preparation

Multi-Brønsted acidic ionic liquids were prepared following the procedure outlined in literature [17, 18]. The detailed preparations were as follows: hexamethylenetetramine (Qiangsheng Function Chemistry Co., Ltd., Jiangsu, China) (0.1 mol) and 1,3-propane sultone (Wuhan Sail Chemical Co., Ltd., China) (0.4 mol) were dissolved in tetrahydrofuran (THF) (60 ml), and then stirred continuously for about 48 h at 60°C. After solidification, the zwitterion mass was recrystallized with methanol and ethyl acetate and then dried under vacuum. A stoichiometric amount of H_2SO_4 (0.4 mol) was added to the precursor zwitterions. Then, the mixture was stirred at 90°C for 12 h. After the reaction, the obtained viscous liquid was washed with toluene three times and dried in a vacuum (Shanghai Boxun Industrial Co., Ltd., China) to form ionic liquid (N,N′,N″,N‴-tetrapropane sulfonic hexamethylenetetramine

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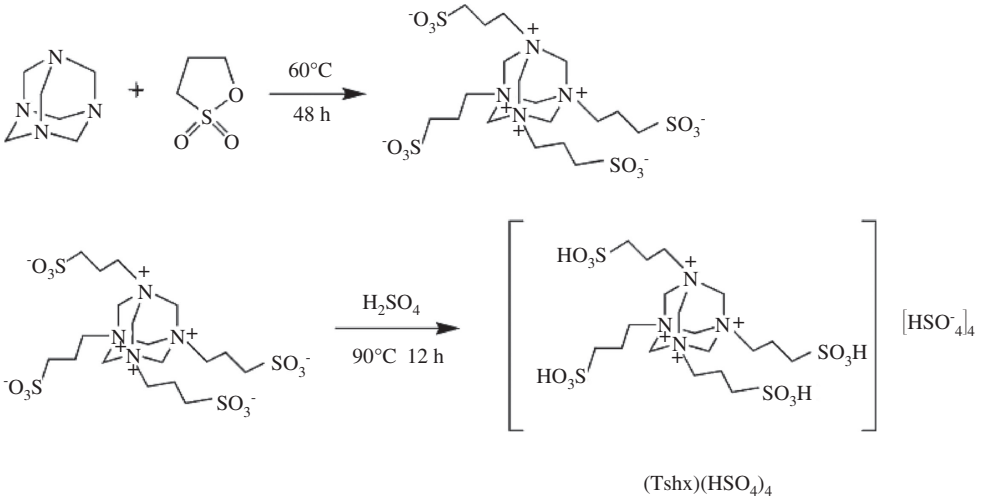
tetrahydrosulfate). The catalyst was abbreviated as $(Tshx)(HSO_4)_4$. The synthesis procedures of other ionic liquids were similar to $(Tshx)(HSO_4)_4$. All the chemicals were research grade and were used without further purification unless otherwise stated. The formation of $(Tshx)(HSO_4)_4$ reaction is based on the following equation:



$(Tshx)(HSO_4)_4$

2.2 Catalyst characterization

The ionic liquids were characterized by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy using a Bruker AV500 spectrometer in D_2O. Fourier transform infrared spectroscopy (FT-IR) spectra (Bruker Optics) for samples in KBr disks were performed on a Bruker IFS28 spectrometer. Thermogravimetric and differential thermogravimetric (TG-DTG) curves were measured on a TG209 (NETZSCH) thermal analyzer at a heating rate of 10 K/min under the protection of nitrogen.

^1H NMR (500 MHz, D_2O, TMS): δ 1.904 (m, 8H), 2.808 (t, 8H), 2.946(t, 8H), 4.680 (s, 12H); ^{13}C NMR (500 MHz, D_2O): δ17.34, 49.14, 57.04, 79.99 ppm; IR (KBr): 3440.66, 2967.51, 2928.51, 1631.72, 1432.51, 1240.13, 1176.83, 1074.40, 1041.57, 881.03, 855.69, 610.02, 582.63 cm^{-1}. The thermal decomposition point was 293.3°C.

2.3 UV-visible acidity evaluation

The measurement of the Hammett acidity of different Brønsted acidic ionic liquids was conducted on the UV-visible spectrophotometer (Shimadzu) in the presence of a basic indicator. The Hammett acidity of each sample was calculated with the formula:

$$H_0 = pK(I)_{aq} + \log_{10}([I]/[HI^+]) \quad (1)$$

where $pK(I)_{aq}$ is the pK_a of the indicator, I refers to the indicator base and $[I]$ and $[HI^+]$ represent the molar concentrations of the unprotonated and protonated forms of indicator, respectively. The results are presented in Table 1.

2.4 Catalytic testing

The typical esterification procedure followed was: methanol, *n*-caprylic acid and catalyst were placed in a 100 ml three-necked flask. The flask was equipped with a dropping funnel including 3A mesoporous molecular sieves for removing the water of the system with a reflux condenser. The reaction mixture was heated to reflux (oil bath) for the desired time under mechanical stirring and then cooled to room temperature. Subsequently, the layers separated.

Table 1 Hammett function values of various acidic ionic liquids[a].

Ionic liquids	A_{max}	[*I*] (%)	[*HI*+] (%)	H_0
4-Nitroaniline	1.977	100.0	0.0	–
$(Tshx)(HSO_4)_4$	1.542	78.0	22.0	1.54
$(Dspi)(HSO_4)_2$	1.752	88.6	11.4	1.88
$(HSO_3\text{-pmim})HSO_4$	1.852	93.7	6.3	2.16

[a]Ionic liquids and the indicator 4-nitroaniline were dissolved in H_2O at concentrations of 5×10^{-3} mol/l and 1.5×10^{-4} mol/l, respectively; Indicator: 4-nitroaniline (NA) [pK(I)aq=0.99].
$(Tshx)(HSO_4)_4$=(N, N′, N″, N‴-tetrapropane sulfonic hexamethylenetetramine tetrahydrosulfate); $(Dspi)(HSO_4)_2$ (Dspi=N, N′-dipropane sulfonic piperazine); $(HSO_3\text{-pmim})HSO_4$=1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate.

The upper layer was ester, and the ionic liquid catalyst appeared in the lower liquid phase. Chemical analysis of the products was performed by gas chromatography (Agilent 6890N GC), equipped with an HP-5 capillary column and an flame ionization detector. Reactants and products were identified by comparison with authentic samples. Methyl laurate was used as the internal standard.

2.5 Kinetic studies

A detailed kinetic study was employed for the esterification reaction of methyl caprylate with caprylic acid and methanol at different temperatures (323 K, 333 K, 343 K, 353 K, 363 K) and different reaction times (0–150 min). Kinetic parameters were investigated under the given optimum parameters (amount of catalyst of 2.25%, methanol/caprylic acid molar ratio of 7.5). The reaction rate equation was defined as:

$$r = -\frac{dC_A}{dt} = k_+ C_A^{\alpha} C_B^{\beta} - k_- C_C^{\gamma} C_D^{\eta} \quad (2)$$

where C_A, C_B, C_C and C_D present the concentrations of caprylic acid, methanol, methyl caprylate and water, respectively, k_+ and k_- are the forward and reverse rate constants, respectively, and α, β, γ and δ are the reaction order of caprylic acid, methanol, methyl caprylate and water, respectively. Given that the reaction was carried out using 3A mesoporous molecular sieves to remove the water generated from esterification, the esterification process could be considered irreversible in this study. The concentration of methanol could be regarded as constant because of the excessive presence of it. Thus, five sets of runs for kinetic models were performed. The reaction rate equation was defined as:

$$r=-\frac{dC_A}{dt}=kC_A^{\alpha} \quad (3)$$

where $k=k_+C_B^{\beta}$. After a series of calculations, the values of k and α for the esterification reaction at different temperatures could be obtained. The Arrhenius equation, which was used to determine and describe the reaction system, was defined as:

$$\ln k=-E_a/RT+\ln k_0 \quad (4)$$

where R represents the gas constant and T is the temperature. Activation energy (E_a) is often used to determine the minimum amount of energy for the esterification reaction.

3 Results and discussion

3.1 Determination of H_0 values and comparison of the activities of ionic liquids

Catalytic esterification reactions are influenced by many factors, which include the presence of catalytic activators or poisons, solvent agitation, temperature and other conditions specific to the particular process. One of the more important considerations is the acidity of the catalyst. Therefore, we obtained the acidity order of the ionic liquids with the following H_0 values (Table 1): (Tshx)$(HSO_4)_4$(1.54)>(Dspi)$(HSO_4)_2$(1.88)>$(HSO_3$-pmim$)HSO_4$ (2.16), suggesting that the ionic liquid with four sulfonic groups exhibited relatively stronger acidity than the other ionic liquids in this work. The acidity of the ionic liquids depended on the characteristics of both the cations and anions. When the anions of the ionic liquids were the same, the dependence of the acidity of the ionic liquid on cations was significant. The catalytic activity of ionic liquids was also investigated, and the results are listed in Table 2. From Table 2, we found the order of activity of ionic liquids was the same as the order of acidity. The ionic liquids with $(Tshx)^{4+}$ cations exhibited stronger catalytic activity, with 91.0% ester yield, even in low amounts than that with $(Dspi)^{2+}$cations and $(HSO_3$-pmim$)^+$ cations, with 88.6% and 85.6%, respectively. Similar results have also been found in other Fish esterification reactions [12].

Table 2 Catalytic performances of different ionic liquids.

Catalyst	Amount of catalyst (mmol)	Yield of methyl caprylate (%)[a]
(Tshx)$(HSO_4)_4$	0.3	91.0
(Dspi)$(HSO_4)_2$	0.6	88.6
$(HSO_3$-pmim$)HSO_4$	1.2	85.6

[a]The reaction conditions: molar ratio of methanol/caprylic acid 7.5:1; reaction temperature 90°C; reaction time 2.5 h. (Tshx)$(HSO_4)_4$=(N, N′, N″, N‴-tetrapropane sulfonic hexamethylenetetramine tetrahydrosulfate); (Dspi)$(HSO_4)_2$ (Dspi=N, N′-dipropane sulfonic piperazine); $(HSO_3$-pmim$)HSO_4$=1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate.

Detailed investigations on esterification were conducted using (Tshx)$(HSO_4)_4$ as a catalyst, since it was also less toxic and expensive, in addition to showing high product selectivity.

3.2 Effects of operating parameters

3.2.1 Effects of amount of (Tshx)$(HSO_4)_4$

Catalyst dosage plays a very important role during the esterification reaction. Finding the optimum catalyst dosage has priority among all reaction parameters, due to its high effectiveness to the whole process. Optimum catalyst dosage also can provide enough active moieties for the esterification reaction. The effect of the amount of catalyst on the esterification of *n*-caprylic acid with methanol is shown in Figure 1. A higher dosage of catalyst in the reaction led to high yield of methyl caprylate.

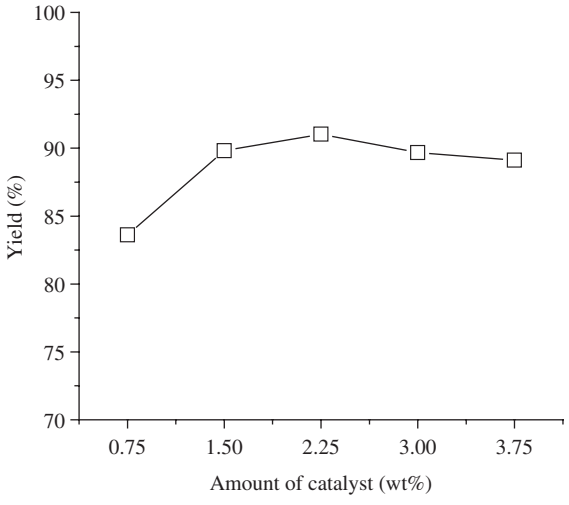


Figure 1 Yield of methyl caprylate by esterification of caprylic acid with methanol over (Tshx)$(HSO_4)_4$ under different amount of catalysts.

However, with the increase of catalyst dosage, the conversion of *n*-caprylic acid decreased slightly. The reason was that the acidity of the reaction system increased with too much acidic catalyst, which improved the side effects. The yield of methyl caprylate decreased.

3.2.2 Effect of reaction time

Generally, conversion of caprylic acid was strongly dependent on the reaction time and an optimum reaction time was needed. As shown in Figure 2, the yield of methyl caprylate increased when the reaction time was prolonged. The highest yield of methyl caprylate reached 92.1% using (Tshx)$(HSO_4)_4$ catalyst at 2.5 h. The rate did not increase obviously from 2.5 h to 3.5 h; this was in fact that the reaction reached the equilibrium. Therefore, the reaction time of 2.5 h was suitable for the esterification reaction over (Tshx)$(HSO_4)_4$ catalyst.

3.2.3 Effect of molar ratio of methanol to caprylic acid

We know that the esterification is a reversible reaction, so excessive alcohol was usually added to improve the yield. From an economic perspective, controlling the molar ratio also results in reducing the overall production cost of methyl caprylate. In the article, the molar ratio was studied in the range 1:1–10:1. Figure 3 shows the effect of different molar ratios of caprylic acid to methanol. Low loading of methanol made the reaction insufficient to decrease caprylic acid content to the target methyl caprylate level.

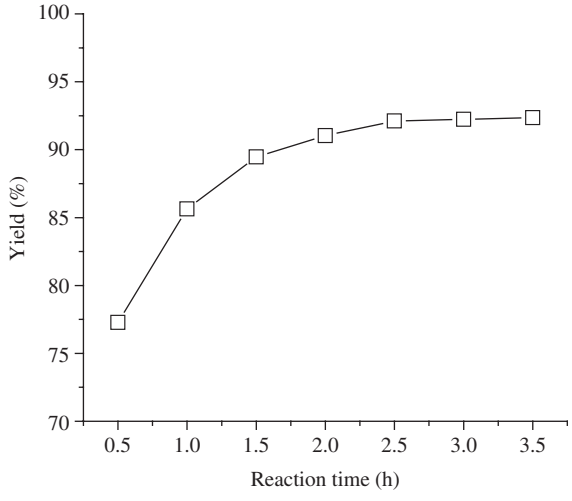


Figure 2 Yield of methyl caprylate by esterification of caprylic acid with methanol over (Tshx)$(HSO_4)_4$ under different reaction times.

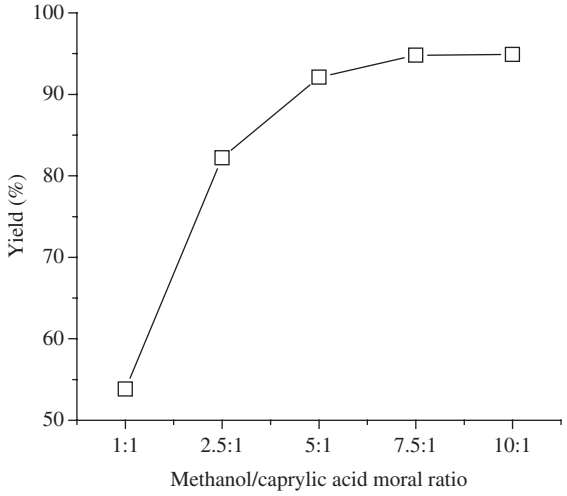


Figure 3 Yield of methyl caprylate by esterification of caprylic acid with methanol over (Tshx)$(HSO_4)_4$ under different methanol/caprylic acid molar ratios.

A high molar ratio provided more opportunity for reactant molecules to collide and then shifted the equilibrium towards the product. For this reaction, we found that the 7.5:1 molar ratio was sufficient to decrease the high caprylic acid content; the yield of methyl caprylate was 94.8%. However, excess molar ratio did not show any improvement in the conversion, probably because caprylic acid was too diluted with excess methanol. Therefore, 7.5:1 was selected as the optimum value for the esterification reaction using (Tshx)$(HSO_4)_4$ catalyst.

3.2.4 Effect of reaction temperature

Furthermore, since water is inevitably formed during esterification, continuous removal of water during the reaction process would be helpful for a high ester yield. In this regard, a 3A molecular sieve was used to remove the water. The influence of different reaction temperatures on the conversion of caprylic acid is shown in Figure 4. The yield of methyl caprylate increased with a rise in temperature; when the reaction temperature reached 90°C, 94.8% of caprylic acid was converted into methyl caprylate in 2.5 h. As compared with the low temperature, the increasing temperature could remove water promptly and the quick reflux accelerated the esterification reaction. However, the yield did not increase obviously with the temperature above 90°C. For reducing the energy consumption, 90°C was chosen as the optimum value for the esterification of caprylic acid with methanol.

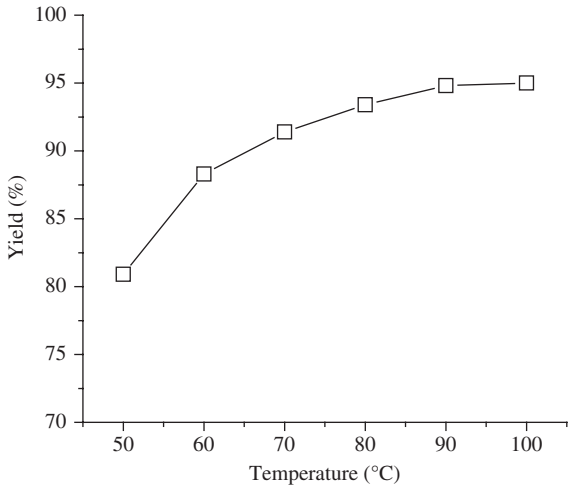


Figure 4 Yield of methyl caprylate by esterification of caprylic acid with methanol over (Tshx)$(HSO_4)_4$ under different temperatures.

3.3 Reuse of the catalyst

One primary advantage of the catalyst was reusability. After each reaction run, the catalyst was washed with toluene and dried in vacuum for 10 h at 70°C to obtain. The yields of the reaction using the recyclable catalyst are shown in Figure 5. It could be seen that the catalyst was repeatedly used six times without obvious drop, further indicating that (Tshx)$(HSO_4)_4$ as catalyst for the esterification was recyclable.

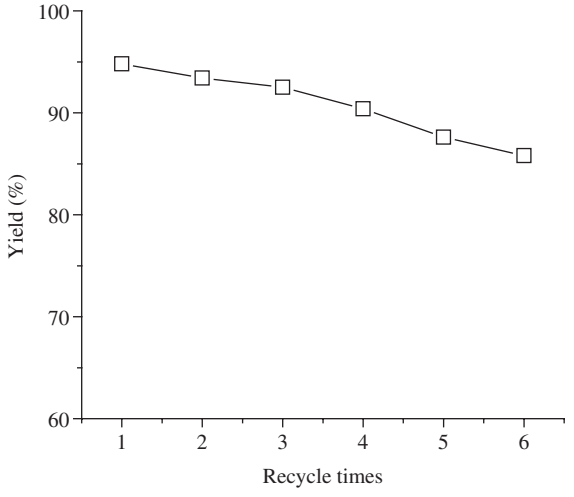


Figure 5 Catalyst recycling in the esterification of caprylic acid with methanol.
Reaction conditions: molar ratio of methanol/caprylic acid 7.5:1, catalyst amount 2.25%, temperature 90°C, and reaction time 2.5 h.

3.4 Kinetic model

The kinetic model of esterification of *n*-caprylic acid to methanol was established over Brønsted acidic ionic liquids (Tshx)$(HSO_4)_4$ and experiments were conducted with amount of catalyst of 2.25% and methanol/caprylic acid molar ratio 7.5. The reactions were performed with the reaction temperatures from 323 K to 363 K and the values of ln k and α shown in Table 3 indicated that the average reaction order for the esterification was 1.54.

The relationship between ln k and $1/T$ is represented in Figure 6, which shows a linear relationship of the reaction rate with respect to time for the reaction and the values of activation energy E_a (kJ/mol) and pre-exponential factor k_0 were determined from the plot using the Arrhenius equation. The equation ln k=-2960.21/T+4.86 reported that the activation energy E_a was 24.61 kJ/mol, and the pre-exponential factor k_0 was 129.40 l/(mol.min). The activation energy value for this esterification catalyzed by (Tshx)$(HSO_4)_4$ was low, which proved that the catalyst worked well on the esterification reaction of caprylic acid with methanol.

Table 3 The kinetic parameters for the esterification of caprylic acid with methanol over (Tshx)$(HSO_4)_4$.

No.	T	ln k	α	R^2
1	323 K	-4.358	1.619	0.98884
2	333 K	-3.959	1.495	0.98238
3	343 K	-3.757	1.465	0.98476
4	353 K	-3.509	1.562	0.98445
5	363 K	-3.326	1.572	0.97254

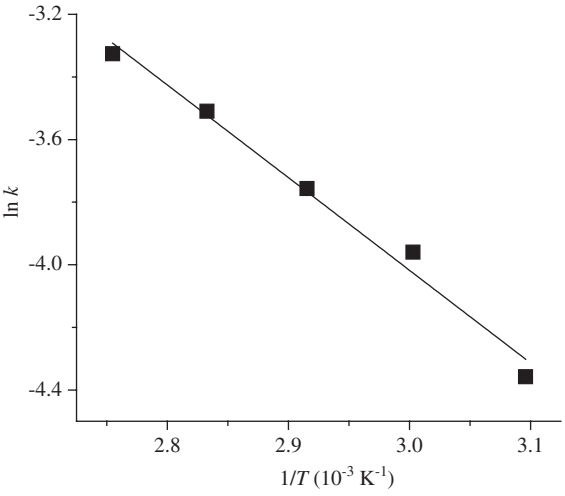


Figure 6 Arrhenius plot of ln k versus $1/T$.

4 Conclusion

The Brønsted acidic ionic liquid with four -SO_3H groups was shown to be efficient for the esterification of caprylic acid with methanol. The high yield of methyl caprylate reached 94.8% under the optimized reaction conditions of amount of catalyst 2.25%, methanol/caprylic acid molar ratio 7.5:1 and reaction time 2.5 h. A kinetic model was established for the esterification of caprylic acid with methanol. By fitting the kinetic model with the experimental results, the reaction order was 1.54 and the activation energy E_a was 24.61 kJ/mol.

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Bionotes

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