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Research Article

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Synthesis of methyl laurate catalyzed by bronsted acid ionic liquids

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ABSTRACT

Ionic liquids as environmentally benign chemical solvent, had been used in diverse chemical reactions, because they have many advantages, such as non-corrosion, non-toxic, non-volatile, anti-oxidize, wide temperature range, good stability, high catalytic activity. Two kinds of Brønsted ionic liquids 1-methylimidazolium hydrogen sulfate ([Hmim]HSO_4) and 1-methyl-2-pyrrolidonium hydrogen sulfate ([Hnmp]HSO_4) were prepared. Synthesis of methyl laurate from lauric acid catalyzed by the ionic liquid was studied. Effects of ionic liquid dosage, molar ratio between methanol and lauric acid, reaction temperature and reaction time on the esterification reaction and stability of the ionic liquid were investigated. Optimal esterification condition was obtained as follows: n(methanol): n(lauric acid) = 6: 1, reaction temperature 70 ℃, reaction time 2 h, dosage of ionic liquid = 5 % of the lauric acid weight. The yield of methyl laurate reached 97.41 % without removal of water during the esterificaion. The ionic liquid was stable and could be repeatedly used.

Keywords: Brønsted acidic ionic liquid, Catalysts, Esterification, Methyl laurate

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INTRODUCTION

Due to the depletion of the world's petroleum reserves and the increasing environmental concerns, there is a great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels [1]. Biodiesel is an "alternative" diesel fuel that is becoming accepted in a steadily growing number of countries around the world [2]. Chemically, biodiesel is a mixture of fatty acid alkyl esters which are produced from a broad range of oil materials, such as vegetable oils, animal fats and waste oil [3]. Chemical transesterification has been used for the industrial production of biodiesel although the process has several drawbacks: it is energy intensive; recovery of the glycerol by-product is difficult; the acidic or alkaline catalyst has to be removed from the product; alkaline waste water require treatment; and both free fatty acid and water interfere in the reaction [4]. In this respect, there are huge scientific and technological efforts to minimize these problems by the development of heterogeneous catalysts, organic bases, methanolysis under supercritical conditions and enzymes [1, 5-8]. But the advent of new solid catalysts, major problems like the use of solvents are separation of glycerol, yield and regeneration of catalysts are still unsolved [9]. In contrast to the common alkali-catalyzed method, supercritical process has advantages in terms of reaction time and purification but requires a high temperature and pressure, hence requiring a high amount of energy [1]. Enzymes are expensive for industrial scale production [10].

ILs are defined as salts that are usually liquid at room temperature due to its melting temperature of below 100℃, and are solely composed of several cations and anions. ILs are eminent and green, suitable to replace conventional solvents in chemical synthesis. Among the unique characteristics of ILs are negligible vapor pressure, good solubility in both organic and inorganic materials, able to form multiple phase systems due to their miscibility, and highly tunable for specific tasks [11-12]. Room-temperature ionic liquids(ILs) have attracted much attention for synthetic and catalytic application because of their important attributes such as wide liquid range, negligible vapor pressure, high catalytic activity, excellent chemical and thermal stabilities, potential recoverability, design possibilities, and ease of separation of the products from reactants [13]. By combining these two advantages of homogeneous and heterogeneous catalysts, application of ILs as catalyst in biodiesel synthesis have started to gain popularity [14]. L. Andreani and J. D. Rocha [15] discusses the feasibility of the use of ionic liquids as catalysts in the biodiesel production field, through the analysis of the data generated in the studies reviewed, it is possible to affirm that ionic liquids present great potential as catalysts for biodiesel production, as immediate advantages, the use of ionic liquids leads to a reduction of the amount of residual water generated in the treatment of biodiesel compared to the traditionally used catalysts and the achievement of processes with fewer steps for product separation and purification. Mohammad Fauzi, A. H., & Amin, N. A. S. [16] presented the properties of ionic liquids, emphasized their versatility as solvents, and the use of switchable ionic liquids as green solvents. They also discussed the roles of ionic liquids in biodiesel synthesis, focusing on their pertinent capability as solvents. But there are some challenges to be faced, such as the production of ionic liquids with low cost, easy recovery and with the possibility of reutilization of the catalyst for several cycles. Ionic liquids are promising catalysts for the production of biodiesel， which meet the requirements of green chemistry showing attractive prospect for industrialization [14]. Han *et al* [17-20] reviewed Brønsted acid ionic liquids, Lewis acid ionic liquids and base ionic liquids as environmentally friendly catalysts in biodiesel production.

Fatty acid methyl ester plays an important role in the oil chemical industry. Methyl can substitute fatty acid as many oil chemical raw material, such as chemical intermediates useful for fatty alcohols, alkyl alcohol amide, α-sulfonated methyl and so on [21]. On the other hand, FAME is a substitute of diesel [22]. Lauric acid methyl ester is a kind of colorless transparent liquid with a sweet. It is raw material of synthesis of lauric acid sucrose ester, a variety of anionic surfactant and nonionic surface active agent. It is an important intermediate in the fine chemical industry [23]. In generally, methyl laurate was synthesize by lauric acid and methanol direct esterification with sulfuric acid as catalyst, there are serious equipment corrosion, many side reactions, the yield is not high, difficult separation, a series of environmental pollution and other issues [24]. Xu *et al* [25] synthesized methyl laurate using sulfonate DNW-1 resin as catalyst, the esterification rate reached to 94.6%. But the reaction process needed a large amount of catalyst, long reaction time, easy be carbonized resin at the end of the reaction, resulting in inactivation. Li *et al* [26] synthesized methyl laurate using SG-SAZnA as catalyst, the conversion of lauric acid achieved 75%, after the catalyst reused for 5 times, the conversion could still achieved 73.18%. Because of the esterification rate is low, this process is not conducive to industrial production. Chen *et al* [27] synthesized methyl lautrate from lauric acid and methanol in the present of $CePW_{12}O_{40}$ catalyst, the experimental results showed that the catalyst exhibited good catalytic activity after recrystalli-zation and recycling many times, and lauric acid coversion of above 97.0% was attained under the optimum experiment-al condition, but the catalyst regeneration processing was complex.

In this work, the new catalytic reaction system of synthesis of methyl laurate was studied, two kinds of Brønsted ionic liquids 1-methylimidazolium hydrogen sulfate ([Hmim]HSO_4) and 1-methyl-2-pyrrolidonium hydrogen sulfate ([Hnmp]HSO_4) were prepared. And the utilization of Brønsted acid ionic liquids as catalyst on lauric acid esterification was described. The comparison between it's catalytic activity and those of the traditional Bronsted acids on ethanol esterification reactions that Brønsted acid ionic liquids is a lot more advantage than other catalysts. In addition to that, the Brønsted acid ionic liquids can be recovered and reused without catalytic activity loss via simple and efficient recycle protocols. The effects of reaction variables such as effects of ionic liquid dosage, molar ratio between methanol and lauric acid, reaction temperature and reaction time on the esterification reaction and stability of the ionic liquid were investigated.

EXPERIMENTAL SECTION

2.1 Materials and Apparatus

All reagents were obtained from commercial sources and used without further purification. N-Methylimidazole(AR, 99%), 1-Methyl-2-pyrrolidone (AR, 99%), concentrated sulfuric acid(AR, 98%), acetonitrile(AR), ethyl acetate(AR), ethyl ether(AR), lauric acid(AR), methanol(AR), ethanol (95%, industrial grade), KOH(AR), two potassium acid phthalate(AR).

Electronic balance (Shanghai Balance Instrument Factory, FA2104), vacuum rotating evaporation instrument (Shanghai Senco machinery Institute, R-501), thermostat water bath (Shanghai Senco machinery Institute, R501), magnetic stirrer(Shandong Juancheng Guangming Yiqi Co. Ltd, DHT), electric thermostatic drier(Shandong Weifeng Pharmaceutical Group Co. Ltd medical instrument factory, 202), small vacuum pump, etc.

2.2 Preparation of Brønsted Acidic Ionic Liquids

2.2.1 Methylimidazolium hydrogen sulfate [Hmim]HSO_4 [28]

1-Methylimidazole and acetonitrile were charged into a 250 mL round-bottom flask. Then, the mixtures were stirred at 0℃ for 1 min. Then, a stoichiometric amount of concentrated sulfuric acid (98%) was added drop wise and the mixture stirred for 1 h at 0℃ and then stirred for 2 h at room temperature. The Brønsted acidic ionic liquid was washed repeatedly with ether to remove non-ionic residues and dried in vacuum.

2.2.2 1-methyl-2-pyrrolidonium hydrogen sulfate [Hnmp]HSO_4 [29]

In the absence of solvent, 1-Methyl-2-pyrrolidone was charged into a 250 mL round-bottom flask. Then, a stoichiometric amount of concentrated sulfuric acid (98%) was added drop wise at 0℃ and the mixture stirred for 1 h at 0℃ and then stirred for 24 h at room temperature. The Brønsted acidic ionic liquid was washed repeatedly with ethyl acetate to remove non-ionic residues and dried in vacuum.

2.3 General Procedure for Synthesis of Methyl Laurate

Weighed amounts of lauric acids, methanol and ionic liquid were added to a flask having a reflux condenser, and a magnetic stirring apparatus. The esterification reaction was typically carried out for a time at the desired temperature with vigorous stirring. Then the reaction mixture became biphasic, the upper phase, which was mainly the desired methyl laurate, could be isolated simply by decantation; the lower phase, viscous ionic liquid, could be reused after the water in the ionic liquid was removed. The product was directly measured by KOH- EtOH titration, then acid value was calculated. Acid value was calculated using the following formula (1) [30]. Conversion data were based on lauric acids through KOH titration. Conversion of lauric acids was calculated using the following formula (2).

$$X = \frac{c(V_1 - V_2) \times 56.11}{m} \qquad (1)$$

$$Y = \frac{X_0 - X}{X_0} \times 100\% \qquad (2)$$

where

c : concentration of potassium hydroxide standard solution, moL/L;
V_1 : sample consumption of potassium hydroxide solution volume, mL;
V_2 : blank test using potassium hydroxide solution volume, mL;
M : sample quality, g;
56.11 is the molar mass of potassium hydroxide, g/moL;
X_0 is acid value of lauric acid(KOH), mg/g;
X is acid value of ester layer after the completion of the reaction (KOH), mg/g;
Y is conversion of lauric acids, %

RESULTS AND DISCUSSION

3.1 Catalytic Performances of Different Ionic Liquids

The esterification reaction is acid catalysed reaction, the acid strength of catalyst has great effect on the reaction. The catalytic performances of different ILs are given in Table 1, under the conditions of molar ratio of methanol to lauric acid 3:1, catalyst dosage 5% in the weigh of lauric acid, temperature 100℃ and time 4h. Analytical productivity was based on conversion of lauric acid through KOH titration.

Tab. 1 Results of methyl laurate systhesis using different ionic liquids

Entry	Catalysts	Analytical productivity (%)
1	[Hmim]HSO_4	62.83
2	[Hnmp]HSO_4	96.78

It can be seen that, the IL [Hnmp]HSO_4 showed higher conversion rates than IL [Hmim]HSO_4 in our cases. Secondly, the costs of N-methyl-2-pyrrolidone as a source of cations are more economical than those of 1-methylpyrrolidine and 1-methylimidazole [31]. Furthermore, the preparation of [Hnmp]HSO4 was very easy. So [Hnmp]HSO_4 was further investigated as a catalyst for the esterification of lauric acid with methanol.

3.2 Catalytic activity of [Hnmp]HSO_4 for esterification of lauric acid

3.2.1 Effect of amount of [Hnmp]HSO_4 on lauric acid conversion

Fig. 1 shows the effect of the amount of [Hnmp]HSO_4 on lauric acid conversion (reaction conditions: n (lauric acid) : n (methanol) = 1: 3; reaction temperature = 100℃; reaction time = 4 h.). The amount of ionic liquid had a remarkable effect on the rate of esterification. When 5 wt.% of [Hnmp]HSO_4 was added, 95.85% of lauric acid was converted into methyl laurate in 4 h. But, with the increase in the amount of catalyst, the conversion rate did not significantly increase. So the optimum amount of [Hnmp]HSO_4 was 5 wt.%.

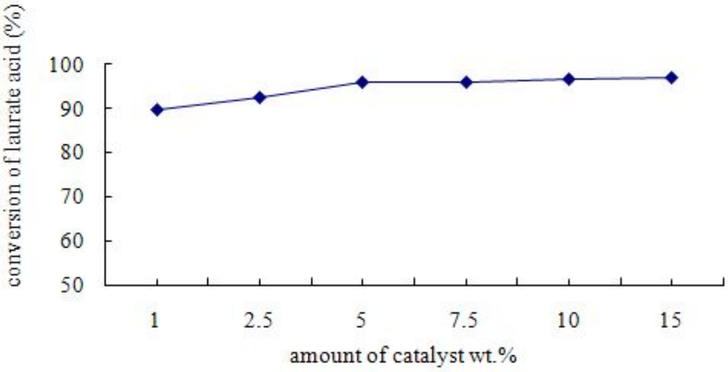

Fig. 1 Effect of the amount of [Hnmp]HSO_4 on lauric acid conversion

3.2.2 Effect of ratio of methanol to lauric acid on lauric acid conversion

An excess of reactant methanol is necessary for the esterification of lauric acid because it can increase the rate of methanolysis. The mole ratio of methanol to lauric acid varied from 1:1 to 9:1, and the conversions obtained are shown in table 2. The more the methanol was added, the higher the conversion of lauric acid to methyl laurate was obtained in the same reaction time. The highest conversion of lauric acid achieved was 96.77% with methanol to lauric acid mole rate of 6:1 in 4 h. Further increase of this mole ratio did not result in an increase in the conversion probably because lauric acid and IL were too diluted with excess methanol. This was in a good agreement with the literature reported earlier [32].

Tab. 2 Effect of ratio of methanol to lauric acid on lauric acid conversion

Entry	n(lauric acid) : n(IL)	Conversion of lauric acid (%)
1	1 : 1	69.35
2	1 : 3	95.85
3	1 : 6	96.77
4	1 : 9	94.38

3.2.3 Effect of reaction temperature on lauric acid conversion

The effect of reaction temperature on lauric acid conversion is shown in Fig. 2. When the reaction temperature was 55℃, 89.15% of lauric acid was converted into methyl laurate in 4 h. Esterification yield increased with a rise in temperature, reaching a maximum of 97.11% in 4 h at 70℃. When the temperature is higher, lauric acid conversion had not decreased significantly. Considering the energy consumption, so the optimum reaction temperature was 70 ℃.

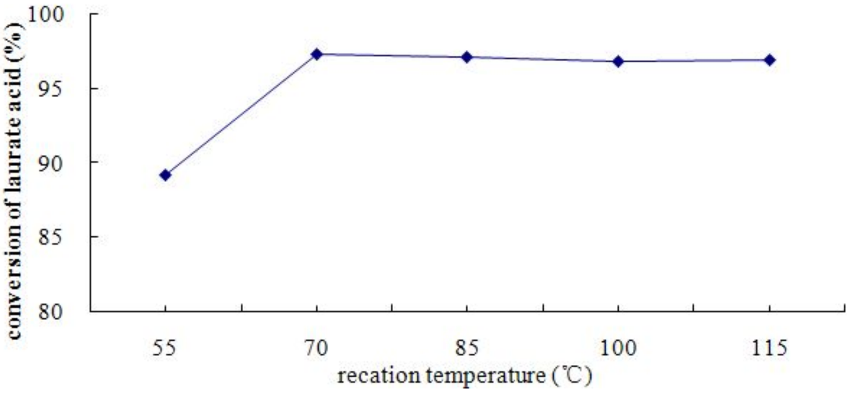

Fig. 2 Effect of reaction temperature on lauric acid conversion

3.2.4 Effect of reaction time on lauric acid conversion

The effect of reaction time on lauric acid conversion is shown in table 3. Esterification yield increased with the increase of reaction time, reaching 97.41% in 2 h at 70℃. As can be seen from the reaction process, exceed 97% of lauric acid was converted into methyl laurate within 2 h, so it was easy for the excess of methanol to react with oleic acid. Along with the extending of reaction time, the conversion of lauric acid had obviously no increase from 2 h to 8 h. This showed that the reaction of methanolysis approached equilibrium after 2 h, and the conversion of lauric acid did not increase when the reaction time was prolonged. Therefore, the best reaction time was 2 h.

Tab. 3 Effect of reaction time on lauric acid conversion

Entry	Reaction time (h)	Conversion of lauric acid (%)
1	1	96.70
2	2	97.41
3	3	97.35
4	4	97.34
5	5	97.44
6	6	97.36
7	7	97.21
8	8	97.18

3.2.5 Reusability of [Hnmp]HSO_4 for esterification of lauric acid

In order to investigate the possibility of recycling of the IL [Hnmp]HSO_4, a recycling experiment was conducted under optimum conditions. The reuse performances of the IL [Hnmp]HSO_4 are shown in Table 4. After esterification, ionic liquid was separated and dried by rotary evaporation, then was reused to esterification of lauric acid. As the ionic liquid's viscosity is high, recovery will have a loss, the loss would be added to the initial quality. [Hnmp]HSO_4 could be reused five times and the conversions of oleic acid were not less than 95.0%, and no obvious change in the property of ionic liquid could be observed. This indicates that the IL catalyst was recyclable and thermally stable for the esterification.

Tab. 4 The conversion of lauric acid using reused ionic liquids

Run	Reaction temperature (℃)	Reaction time (h)	Conversion of lauric acid (%)
1	70	2	97.41
2	70	2	97.23
3	70	2	97.05
4	70	2	96.95
5	70	2	95.89

The production of lauric acid methyl ester may be accomplished by using catalysts [Hnmp]HSO_4. The halogen-free Brønsted acidic ionic liquid [Hnmp]HSO_4 is non-flammable, easy to be synthesized, thermally stable, and exhibits negligible vapor pressure (non-volatile) [32]. For the synthesis of lauric acid methyl ester, Brønsted acidic ionic liquid [Hnmp]HSO_4 show better catalytic and reuse performances. The reaction conditions were optimized through single factor experiment. When the amount of catalyst was 5% of the mass of the lauric acid, methanol to oil molar ratio was 6: 1, reaction temperature 70 ℃ and reaction time 2 h, the lauric acid esterification rate reached 97.41%. And the reaction product and the catalyst was easily separated, catalytic activity without significant decrease after 5 times. The catalytic activity is close to the concentrated sulfuric acid as catalyst [33]. but the reaction product and catalyst were difficult to be separated and reuse, and had corrosion to equipment [34].

CONCLUSION

The ionic liquid [Hnmp]HSO_4, as an esterification catalyst, efficiently promotes the lauric acid esterification with methanol at mild temperature, and esterification reaction could be occur in high yields and in short reaction times. The esters produced could be isolated conveniently in high yields and purity. The ionic liquid [Hnmp]HSO_4 shows good catalytic performance. Esterification of lauric acids and methanol could give satisfied yields of 97.41% under optimal reaction conditions, also [Hnmp]HSO_4 is recyclable. On the other hand, reparation of Brønsted acid ionic liquid [Hnmp]HSO_4 is very easy and the cost is low. Therefore, the use of [Hnmp]HSO_4 will reduce the production costs. An environment-friendly approach for the synthesis of lauric acid methyl ester is provided.

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