

Article

Caprolactam-Based Brønsted Acidic Ionic Liquids for Biodiesel Production from Jatropha Oil

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Abstract: Caprolactam-based ionic liquids show many advantages, such as the lower toxicity, lower cost, and a simple preparation process. In this work, caprolactam-based ionic liquids were prepared and adopted as catalysts for the transesterification of Jatropha oil with methanol. The results demonstrated that the SO₃H-functional caprolactam-based ionic liquids have higher catalytic activity than those of the caprolactam-based ionic liquids without sulfonic group or the SO₃H-functional pyridine-based ionic liquids, attributed to their stronger Brønsted acidity. By optimizing the reaction parameter, the biodiesel yield catalyzed by 1-(4-sulfonic group) butylcaprolactamium hydrogen sulfate ([HSO₃-bCPL][HSO₄]) could reach above 95% at 140 °C for 3 h. Furthermore, the ionic liquid had a good reusability.

Keywords: biodiesel; caprolactam-based ionic liquid; transesterification; acidity

1. Introduction

Biodiesel consisting of fatty acid methyl esters (FAME) has attracted increasing attention as a renewable diesel fuel attributed to its lower pollution emissions and availability from renewable resources such as vegetable oils, animal fats, or waste cooking oil [1,2]. The main technique used to produce biodiesel is the transesterification of triacylglycerols from oils or fats with alcohols catalyzed by acid or base catalysts [3–6].

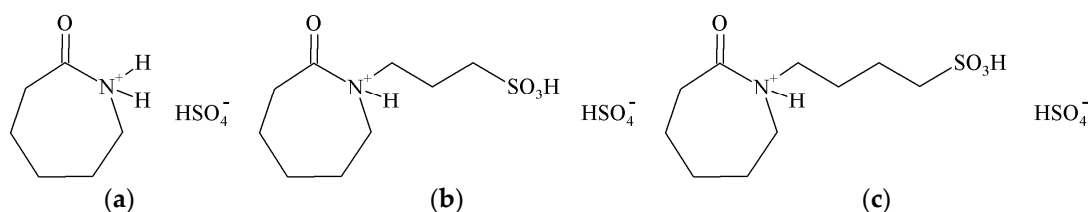
In recent years, ionic liquids (ILs)—especially functionalized acidic ones—have gained significant attention, and numerous have been applied to transesterification for the production of biodiesel. For example, triethylammonium ILs, imidazolium ILs, and pyridinium ILs functionalized by SO₃H group were introduced by Wu et al. for the transesterification of cottonseed oil [7], and it is suggested that pyridinium ILs with SO₃H group exhibited the best catalytic performance. Pyridinium IL possessing the SO₃H group was also prepared by Han et al., and it could be used for the transesterification of waste oil with methanol to give a FAME yield of 93.5% under optimum conditions [8]. After that, Li et al. synthesized a series of pyridinium ILs with SO₃H group, and applied them for the transesterification of Jatropha oil, and the FAME yield could reach 92.0% in the presence of [BSPy]CF₃SO₃ [9]. Likewise, the SO₃H-functional ILs based on benzimidazole synthesized by Ghiaci et al. could be used in the transesterification of canola oil to provide a FAME yield of more than 95% [10]. Li et al. introduced the SO₃H-functional imidazolium IL [BSO₃HMIM]HSO₄ with various metal sulfates [11], and found that [BSO₃HMIM]HSO₄–Fe₂(SO₄)₃ had a superior catalytic activity for the transesterification of *Camptotheca acuminata* seed oil.

As noted above, the SO₃H-functional Brønsted acidic ILs were very efficient for the transesterification. Among these functionalized ILs, the most extensive attention has been focused on imidazole-based or pyridine-based ILs. However, the imidazole- and pyridine-based ILs suffer some

disadvantages for industrial application, such as high cost, difficult preparation, and high toxicity [12,13].

Lactam and its derivatives can be formed by the ammonium cation of IL through acid–base neutralization reaction. Compared with imidazole or pyridine, they are relatively cheaper, less toxic, and easily available from industry [14]. Du et al. reported a series of lactam-based Brønsted acid ILs by neutralization reaction between caprolactam or butyrolactam and inorganic acids which could be applied as replacements of inorganic acids [15]. Caprolactam-based ILs, [Caprolactam] X ($X^- = p\text{TSO}^-$, BSO^- , BF_4^- , NO_3^-), were employed by Qi et al. for the nitration of aromatics nitrate with NO_2/air under mild conditions [16]. Zhang et al. presented the synthesis of caprolactam-based Brønsted acidic ILs such as caprolactam benzenesulfonate, caprolactam hydrosulfate, and caprolactam p-toluenesulfonate, and an application for the regioselective mononitration of chlorobenzene [17]. Huang et al. developed the caprolactam hydrogen sulfate ([CPL] HSO_4) IL and metal halide as the co-catalyst for the efficient production of 5-hydroxymethylfurfural [18]. The cation core of these caprolactam-based ILs was limited to caprolactamium, and was not assembled by other functional groups. Recently, our group developed a SO_3H -functional caprolactam-based IL [19] which exhibited better catalytic performance than that of SO_3H -functional imidazole-based or pyridine-based ILs for the hydrolysis of vegetable oils. However, the application of the caprolactam-based ILs for biodiesel production has still rarely been reported in the literature.

In this work, three kinds of caprolactam-based ILs (as shown in Scheme 1) were prepared, and their acidity was investigated by the UV–visible spectroscopy combined with Hammett acidity function. Then, these ILs were adopted as catalysts for the transesterification of *Jatropha* oil with methanol.



Scheme 1. Structures of the caprolactam-based Brønsted acidic ionic liquids (ILs) adopted in this work: (a) caprolactam hydrosulfate, [CPL] $[\text{HSO}_4]$; (b) 1-(3-sulfonic group) propylcaprolactamium hydrogen sulfate, $[\text{HSO}_3\text{-pCPL}][\text{HSO}_4]$; (c) 1-(4-sulfonic group) butylcaprolactamium hydrogen sulfate, $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$.

2. Results and Discussion

2.1. Acidity Determination of the ILs

The main property of the Brønsted acidic ILs is acidity, which will help establish an appropriate path of the acid-catalyzed reaction. The acidity strength of an acid can be expressed by Hammett function using UV–visible spectrophotometry. For example, the acidity measurement of nonchloroaluminate ILs had been performed successfully utilizing UV–visible spectroscopy with Hammett indicator method [20], and this method was applied to determine the acidity of protic pyridinium ILs, Brønsted acidic ILs, and the strength of carboxylic acids in different ILs [21–24].

A series of solutions for the ILs (10–100 mmol/L) and 4-nitroaniline in methanol were examined, and the absorption spectra of 4-nitroaniline in IL-methanol solution (10 mmol/L) is shown in Figure 1 as the representatives. From the figure, it is evident that the maximal absorbance of the unprotonated form of 4-nitroaniline appeared at 380 nm. The Hammett acidity function (H_0) could be calculated as illustrated in Figure 2 by determining the molar ratio of the unprotonated and protonated forms of 4-nitroaniline in the ILs solutions from the measured absorbances at 380 nm. The IL with lower H_0 value exhibited stronger acidity.

The results in Figure 2 show that the H_0 value of the ILs follows the order of $\text{H}_2\text{SO}_4 \approx [\text{CPL}][\text{HSO}_4] > [\text{HSO}_3\text{-pCPL}][\text{HSO}_4] > [\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ at each concentration. Therefore, the

acidity order of the ILs in the present experimental conditions could be obtained as: $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4] > [\text{HSO}_3\text{-pCPL}][\text{HSO}_4] > [\text{CPL}][\text{HSO}_4] \approx \text{H}_2\text{SO}_4$. These results demonstrated that the cation core of caprolactam assembled by sulfonic group can result in a stronger Brønsted acidity. For the SO_3H -functional caprolactam-based ILs, the sulfonic group with a longer carbon chain results in a stronger acidity.

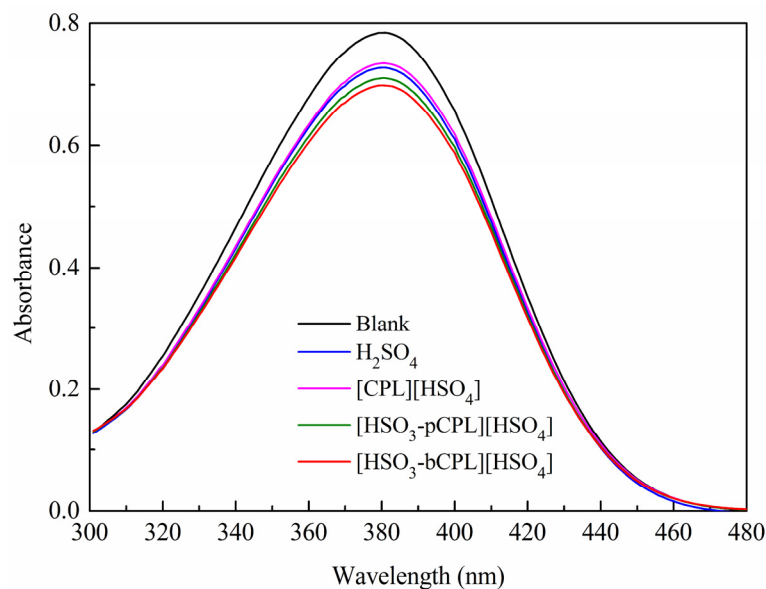


Figure 1. Absorption spectra of 4-nitroaniline for various ILs in methanol.

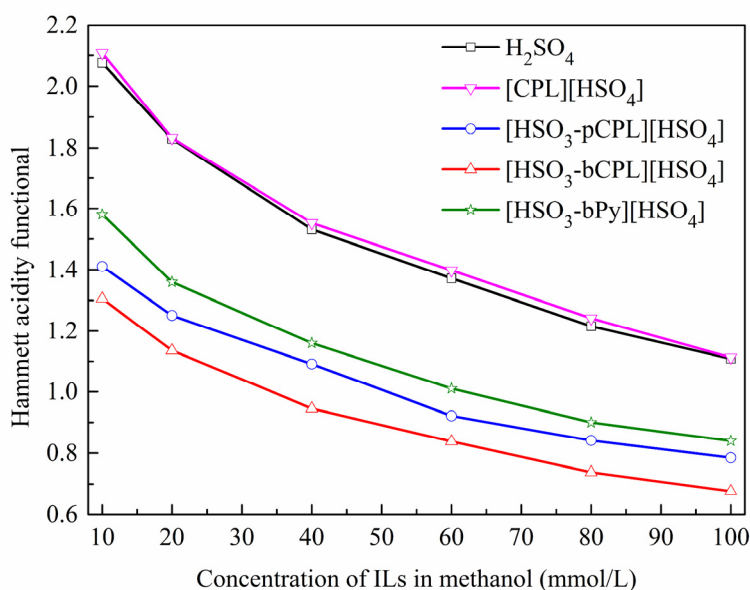


Figure 2. Hammett acidity functional (H_0) of the ILs in methanol with 4-nitroaniline as indicator.

Furthermore, as a typical SO_3H -functional pyridine-based IL, 1-(4-sulfonic group) butylpyridinium hydrogen sulfate ($[\text{HSO}_3\text{-bPy}][\text{HSO}_4]$) was adopted for comparison with the caprolactam-based ILs in this work. These results clearly suggest the stronger acidity of $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ and $[\text{HSO}_3\text{-pCPL}][\text{HSO}_4]$ as compared to that of $[\text{HSO}_3\text{-bPy}][\text{HSO}_4]$.

2.2. Catalytic Test of the ILs

The transesterification of Jatropha oil with methanol catalyzed by different ILs or concentrated sulfuric acid was carried out at a temperature of 100 °C and a methanol/oil/IL (molar ratio) of 6/1/0.2 (see Figure 3). As shown in Figure 3, the cations of ILs had an obvious influence on their catalytic performance. The SO₃H-functional caprolactam-based ILs could provide a better biodiesel yield, and the catalytic performance of the ILs was in the sequence [HSO₃-bCPL][HSO₄] > [HSO₃-pCPL][HSO₄] > [HSO₃-bPy][HSO₄] > [CPL][HSO₄] ≈ H₂SO₄.

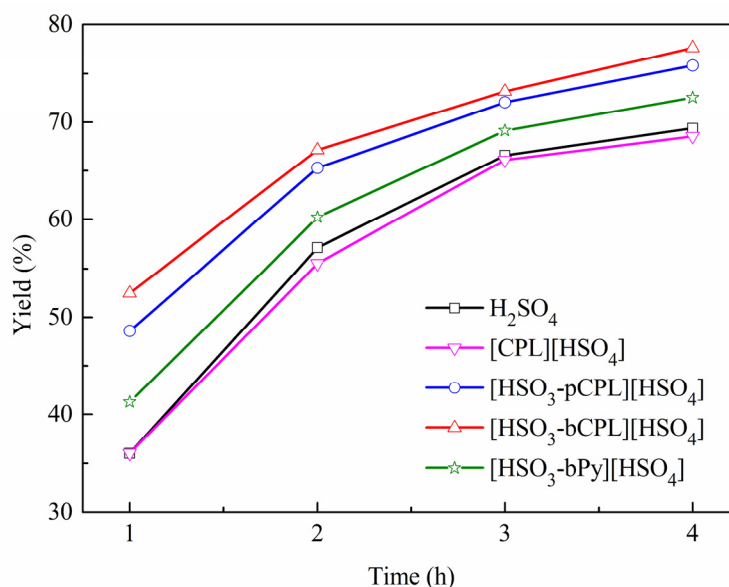
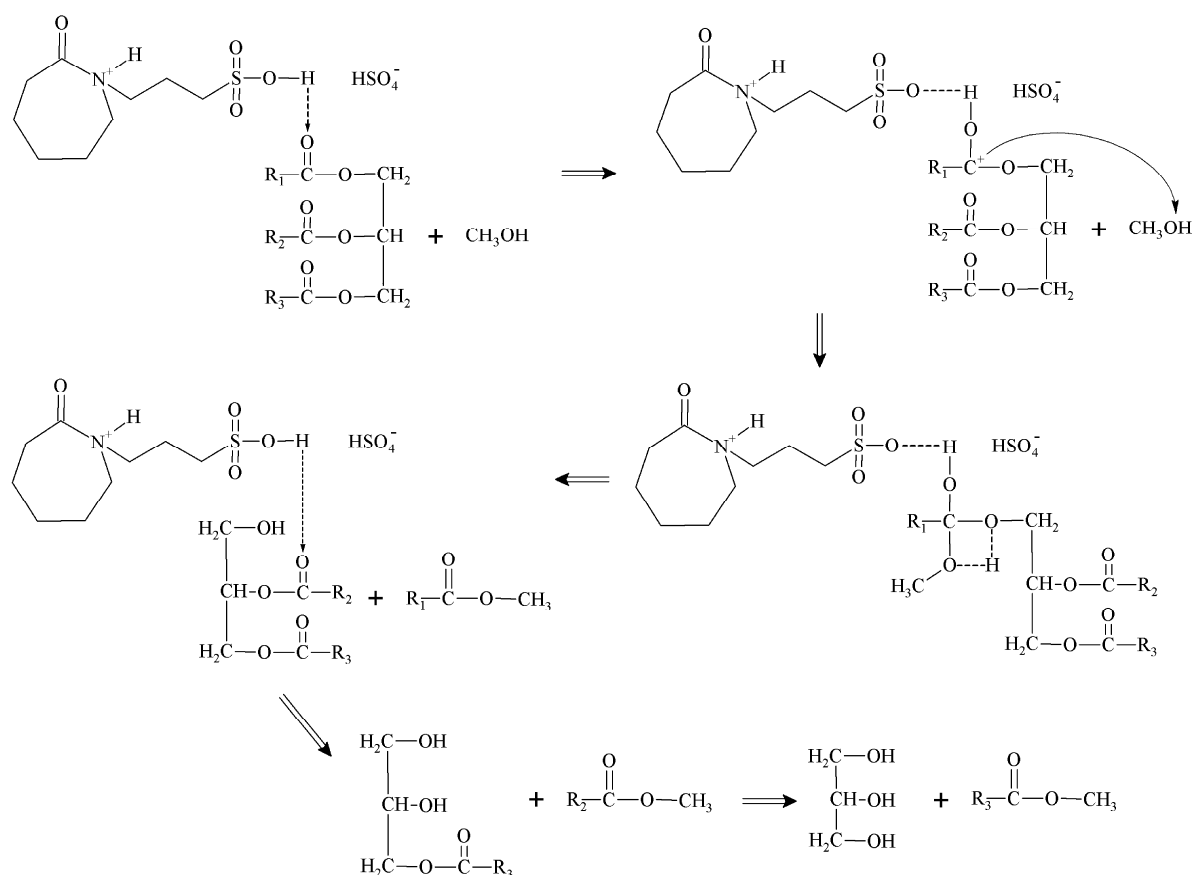


Figure 3. Effect of the ILs on the transesterification of Jatropha oil with methanol. Reaction conditions: temperature = 100 °C, methanol/oil/IL (molar ratio) = 6/1/0.2.

The transesterification is composed of three stepwise and reversible reactions, and the triglyceride is transformed stepwise into a diglyceride, a monoglyceride, and finally a glycerol in each step [25]. According to the classical acid-catalyzed transesterification, a possible reaction mechanism for the transesterification in the presence of ILs ([HSO₃-bCPL][HSO₄] as the representative) is depicted in Scheme 2. In the first step, the H proton provided by the sulfonic group of IL attacks the carbonyl group of triglyceride, and the protonated carbonyl group generates a carbocation. Then, a nucleophilic attacking of methanol to the carbocation leads to an intermediate adduct with the H bonds [26,27]. Finally, the intermediate decomposes into FAME, and the catalytic cycle is completed. It is suggested that the catalytic activity of the adopted IL for the transesterification is mainly derived from the sulfonic group, which can provide the H proton. For the Brønsted acidic catalyst, the stronger acidity means it is more ready to provide the H proton, resulting in a higher catalytic activity [28,29]. The acidity measurement of ILs demonstrates that the acidity of the SO₃H-functional caprolactam-based ILs is stronger than those of the caprolactam-based IL without sulfonic group or the SO₃H-functional pyridine-based IL. The SO₃H-functional caprolactam-based ILs also exhibited a better catalytic performance, and the order of catalytic activities of the ILs is consistent with that of the Brønsted acidity. These results confirm that the acidity plays a crucial role in the catalytic activity of the ILs for the transesterification.



Scheme 2. Reaction mechanism of the transesterification in the presence of $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$.

Furthermore, it is necessary to note that the biodiesel yield utilizing $[\text{CPL}][\text{HSO}_4]$ as a catalyst was similar to the case of concentrated sulfuric acid (attributed to the similar Brønsted acidity), but $[\text{CPL}][\text{HSO}_4]$ could show some advantages. For example, it is low-corrosive and is readily separated and recovered from the product mixture. In addition, the preparation of $[\text{CPL}][\text{HSO}_4]$ was very simple and easy compared with the other ILs.

2.3. Reaction Parameter Analysis

As described above, $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ showed the highest catalytic activity for the transesterification among the ILs. Therefore, the reaction conditions for the transesterification catalyzed by $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ were optimized, expressed in molar ratio of methanol/oil, temperature, reaction time, and IL dosage.

The methanol/oil molar ratio effect on FAME yield was investigated at the IL/oil (molar ratio) of 0.25, reaction temperature of $120\text{ }^\circ\text{C}$, and reaction time of 3 h. Theoretically, one mole of triglycerides needs three moles of methanol to produce three moles of methyl esters, and increasing the amount of methanol is beneficial to shift the equilibrium of the reversible transesterification reaction to the right. As illustrated in Figure 4, the biodiesel yield was significantly increased from 72.8% to 90.8% with the increasing of methanol/oil molar ratio from 3:1 to 9:1. However, further addition of methanol/oil molar ratio greater than 9:1 could no longer obviously increase the yield. Thus, the suitable molar ratio of methanol to *Jatropha* oil was preferred as 9:1.

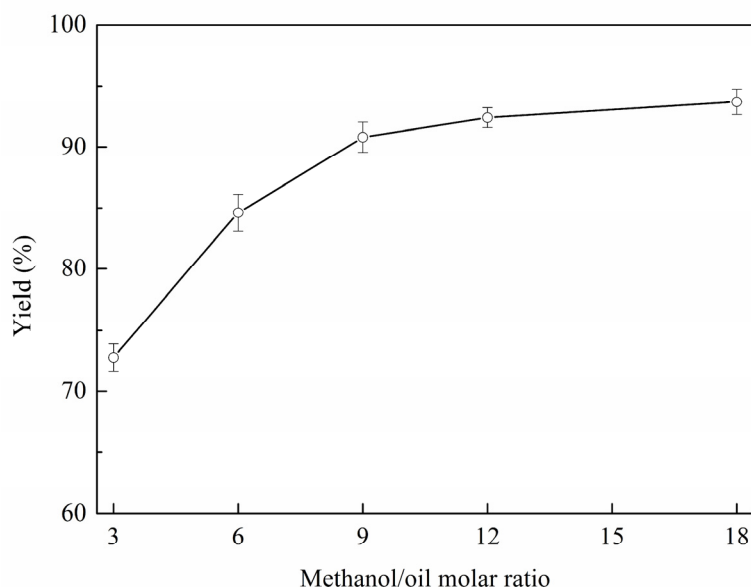


Figure 4. Effect of glycerol/oil molar ratio on the transesterification at a temperature of 120 °C, reaction time of 3 h, and IL/oil molar ratio of 0.25.

Unquestionably, temperature is an important reaction condition for the transesterification. The influence of temperature on biodiesel yield was studied at methanol/oil/IL (molar ratio) of 9/1/0.25 and reaction time of 3 h. As shown in Figure 5, a clear increase of biodiesel yield was observed for increasing temperature from 100 °C to 140 °C. However, the effect of temperature on the biodiesel yield became slight when the temperature was beyond 140 °C. Therefore, the preferable temperature for the transesterification is 140 °C.

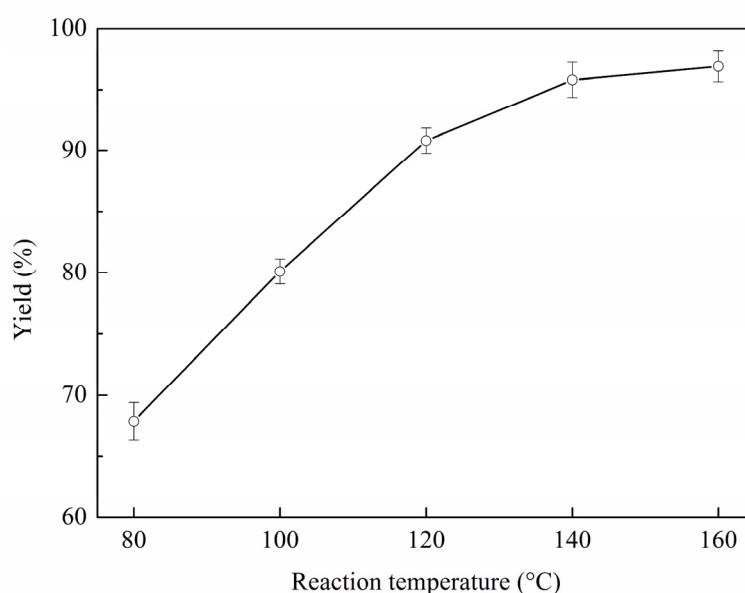


Figure 5. Effect of reaction temperature on the transesterification at reaction time of 3 h and methanol/oil/IL (molar ratio) of 9/1/0.25.

Figure 6 presents the effect of reaction time on the biodiesel yield performed at methanol/oil/IL (molar ratio) of 9/1/0.25 and reaction temperature of 140 °C. As expected, longer reaction time promoted the transesterification reaction, and the yield was raised significantly from 77.3% to 95.8% with an increase of the reaction time from 1 h to 3 h. With further increase of the reaction time from

3 h to 5 h, the yield was almost maintained at about 96%, and the transesterification was close to equilibrium at the reaction time of 3 h. Thereby, the optimal reaction time for the reaction was 3 h.

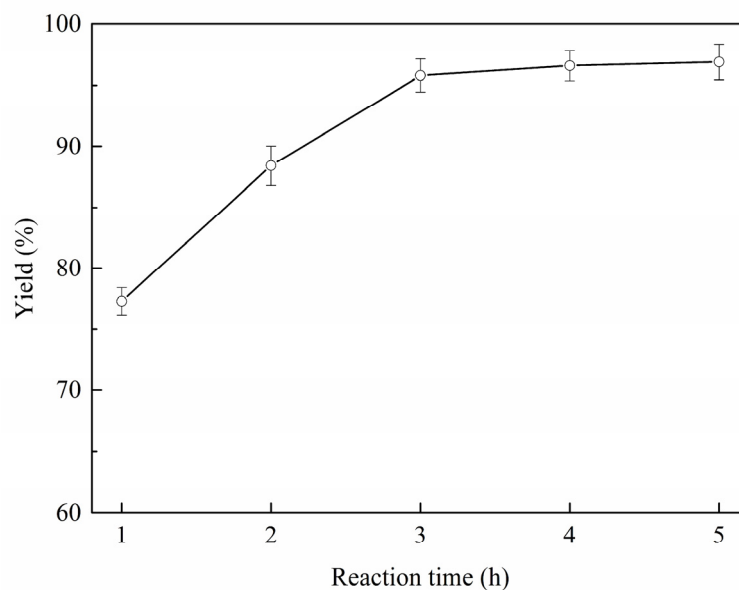


Figure 6. Effect of reaction time on the transesterification at temperature of 140 °C and methanol/oil/IL (molar ratio) of 9/1/0.25.

The effect of IL dosage is clearly significant for the transesterification. The results presented in Figure 7 show that the biodiesel yield increased from 77.5% to 96.9% working at methanol/oil molar ratio of 9:1, temperature of 140 °C, and reaction time of 3 h when the IL dosage (denoted by the molar ratio of IL/oil) was increased from 0.1 to 0.3. However, a slight increase of yield was exhibited when the dosage was beyond 0.20. Therefore, IL/oil (molar ratio) of 0.20 was adopted for the transesterification.

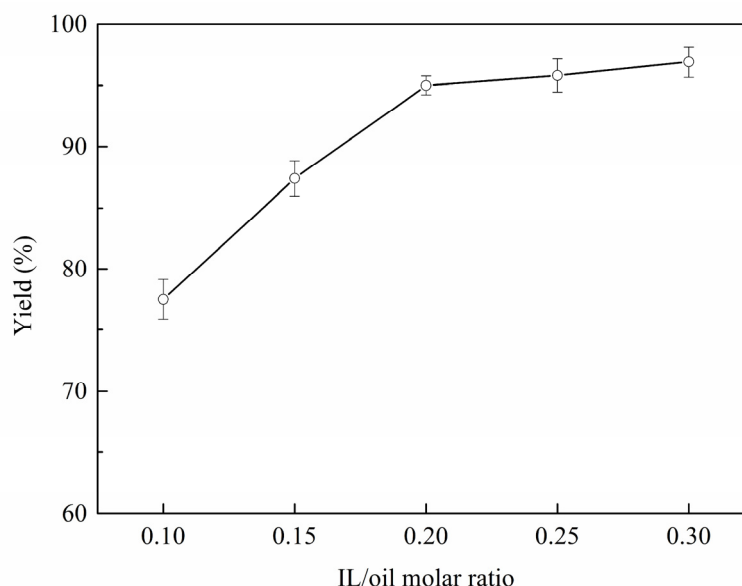


Figure 7. Effect of $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ dosage on the transesterification at temperature of 140 °C, reaction time of 3 h, and glycerol/oil molar ratio of 9.

2.4. Reusability of IL $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$

After the reaction, $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ catalyst was recovered by distillation in vacuum to remove the excess methanol and glycerol, and the recovered catalytic efficiency was investigated at

methanol/oil/IL (molar ratio) of 9/1/0.20, reaction temperature of 140 °C and reaction time of 3 h. The results in Figure 8 show that the biodiesel yield only slightly decreased even after $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ had been reused eight times, suggesting that $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ possesses good stability as a catalyst for the transesterification.

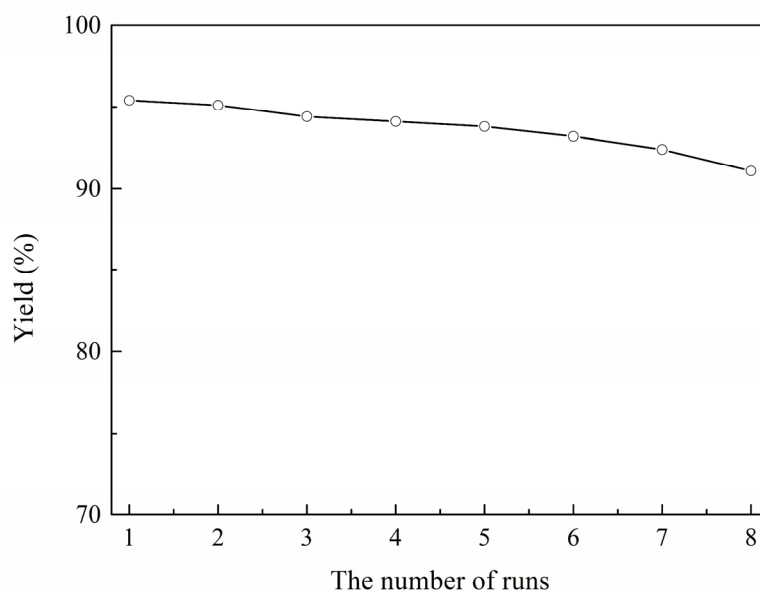


Figure 8. Effect of $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ recycling on the yield. Reaction conditions: temperature = 140 °C, reaction time = 3 h, methanol/oil/IL (molar ratio) = 9/1/0.20.

3. Materials and Methods

3.1. Materials

Caprolactam (AR purity), 1,3-propane sultone (AR purity), 1,4-butane sultone (AR purity), pyridine (AR purity), and sulfuric acid (98%, AR purity) were purchased from Sinopharm Group Co. Ltd. (Beijing, China). Jatropha oil was obtained from China Petroleum Bio-Energy Co. Ltd. (Shenzhen, China). Acid value and saponification value of the Jatropha oil were measured as 21.4 mg KOH/g and 222.8 mg KOH/g, respectively.

3.2. Preparation of Caprolactam-Based ILs

$[\text{CPL}][\text{HSO}_4]$ was prepared by one-step synthesis. Under vigorous stirring, equal-mole concentrated sulfuric acid was dripped slowly into the zwitterions at 80 °C with flowing nitrogen, and the reaction lasted for another 2 h. Then, the product was washed thoroughly with toluene and dry evaporated under vacuum (80 °C) for 4 h, and the stoichiometric IL $[\text{CPL}][\text{HSO}_4]$ was almost obtained.

$[\text{HSO}_3\text{-pCPL}][\text{HSO}_4]$ and $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ were prepared according to the reported procedure [19]. Caprolactam was stirred solvent-free with equal-mole 1,3-propane sultone or 1,4-butane sultone, respectively, at 60 °C for 24 h. The reaction mixture was then washed several times with toluene and dry evaporated under vacuum (80 °C) for 4 h, giving the zwitterion as a white powder. Afterward, equal-mole concentrated sulfuric acid was added dropwise to the zwitterions, and the mixture was vigorously stirred at 80 °C for about 8 h until the zwitterions dissolved. The resultant heavy viscous oil was washed thoroughly with toluene and ether and dry evaporated under vacuum (80 °C) for 4 h to attain the SO_3H -functional caprolactam-based ILs.

3.3. Determination of the Hammett Acidity function

Hammett acidity function (H_0) determined by UV–visible spectroscopy was used for measuring the Brønsted acidity of the ILs. The indicator 4-nitroaniline and the ILs were dissolved in methanol

at the concentrations of 0.072 mmol/L and 10–100 mmol/L, respectively. The UV–vis spectra of the solutions were then recorded on a SPECORD 210 Plus spectrophotometer at room temperature after standing for 6 h. The Hammett acidity function could be calculated by the following formula:

$$H_0 = \text{pK}(\text{B})_{\text{aq}} + \log ([\text{B}]/[\text{HB}]) \quad (1)$$

where $\text{pK}(\text{B})_{\text{aq}}$ is the pK_a value of the indicator (0.99 for 4-nitroaniline), and $[\text{B}]$ and $[\text{HB}]$ are the molar concentrations of the unprotonated and protonated forms of the indicator in the solvent, respectively. Clearly, the low value of H_0 indicates that the IL has a strong acidity. According to the Beer–Lambert law, the value of $[\text{B}]/[\text{HB}]$ can be measured and calculated through UV–vis spectra.

3.4. Biodiesel Production

The transesterification reaction was performed in batch mode using a 250-mL autoclave with a sampling outlet. Jatropha oil, excess methanol, and the IL were poured into the reactor and heated to the reaction temperature at stirring rate of 1500 rpm to eliminate the diffusional limitations. After the reaction, the mixture was cooled to room temperature and separated in a separatory funnel. The upper layer containing FAME was separated from the lower layer consisting of crude glycerol, unreacted methanol, and IL by decantation. The upper layer was then washed several times with hot distilled water and dried by anhydrous sodium sulphate, giving the produced biodiesel.

The yield of biodiesel was defined as a ratio of the weight of FAME determined by Gas Chromatography to the theoretical weights of FAME obtained assuming a 100% conversion of the Jatropha oil, as previously described [30].

4. Conclusions

Caprolactam-based ILs were prepared and adopted as catalysts for the transesterification of Jatropha oil with methanol. The catalytic activities of the ILs were in the sequence $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4] > [\text{HSO}_3\text{-pCPL}][\text{HSO}_4] > [\text{HSO}_3\text{-bPy}][\text{HSO}_4] > [\text{CPL}][\text{HSO}_4] \approx \text{H}_2\text{SO}_4$, which is consistent with the order of the Brønsted acidity determined by Hammett method. The reaction conditions were optimized using $[\text{HSO}_3\text{-bCPL}][\text{HSO}_4]$ as the catalyst, and a biodiesel yield of more than 95% could be obtained at methanol/oil/IL (molar ratio) of 9/1/0.20, reaction temperature of 140 °C, and reaction time of 3 h. Furthermore, the IL possessed a good reusability for the transesterification.

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Author Contributions: H.L. and W.F. conceived and designed the experiments; R.W. performed the experiments; H.Y. and R.W. analyzed the data; G.N. contributed reagents/materials/analysis tools; H.L. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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